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# COMPILATION OF METHODOLOGY FOR MEASURING POLLUTION PARAMETERS OF LANDFILL LEACHATE

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# COMPILATION OF METHODOLOGY USED FOR MEASURING POLLUTION PARAMETERS OF SANITARY LANDFILL LEACHATE

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# FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The Municipal Environmental Research Laboratory contributes to this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This study made an extensive compilation of the different analytical methods used to determine physical, chemical, and biological parameters in solid waste leachate.

# ABSTRACT

The present study made an extensive compilation of the different analytical methods used to determine physical, chemical and biological parameters in solid waste leachate. The compilation was made from information available in the literature and through personal communications with researchers, consulting firms and regulatory agencies.

Since different analytical methods can be used to determine a specific parameter, a preliminary laboratory evaluation was made of those methods least subject to interferences. All analyses were conducted with a relatively concentrated leachate sample obtained from a lysimeter filled with milled solid waste. The results indicate that strong interferences are sometimes encountered when using colorimetric tests due principally to the color and suspended solids present in leachate. In such instances alternative methods were evaluated or recommendations were made to reduce the interfering effects. Automated chemical analysis using colorimetric methods can sometimes experience significant interferences.

Further research is necessary to evaluate additional methods using leachate samples of different strengths and collected from landfills of different ages. The precision and sensitivity of each method will also have to be determined. The interfering parameter should be quantified to allow predictions of its magnitude with leachate samples of different strengths.

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The analytical methods evaluated in the present study for their applicability in leachate analysis are listed in *Standard Methods*, published by the American Public Health Association (APHA) Washington, D.C., and *Methods for Chemical Analysis of Water and Wastes* published by U.S. EPA, Washington, D.C. Permission given by A. Seeber of the APHA to reproduce sections of *Standard Methods* in the present document is greatfully acknowledged. Consultation of both Manuals, however, remains necessary for the successful execution of the chemical analysis.

# SECTION 1

# CONCLUSIONS

It was concluded that samples collected from a recently installed solid waste fill undergo extensive changes of several parameters immediately after collection, unless strict anaerobic sampling and storage conditions are maintained. Preliminary laboratory evaluation of physical, chemical and biological parameters showed that chemical analysis using colorimetric methods is strongly interfered by color, suspended solids and high salt content present in leachate. Interfering effects can be reduced by using a standard addition method in which increasing quantities of the specific parameter are added to the sample after which its recovery is determined. The obtained percentage recovery is then used to readjust the measured value. A less accurate method is to dilute the leachate sample with increasing amounts of dilution water to determine whether the interfering effect can be sufficiently reduced by progressive dilution. One of the above approaches should be used by the analyst prior to the analysis of a series of leachate samples for those parameters most subject to interferences.

An extensive compilation of the different analytical methods used by researchers, consulting firms and regulatory agencies in the U.S.A., showed that numerous methods are used to determine a specific parameter. Based on research conducted at the University of Illinois recommendations were made to use those methods least subject to interference.

# SECTION 2

## RECOMMENDATIONS FOR RESEARCH

The present study conducted a preliminary evaluation of those methods to measure a certain parameter which were least subject to interference. Since only the accuracy of each selected method was evaluated, further research will have to establish the precision and sensitivity. Since all analyses were conducted with a relatively concentrated leachate sample, additional leachate samples of different strength and collected from landfills of different ages, will have to be evaluated.

Methods that are less complicated and time-consuming, but subject to larger interferences than the recommended methods should be evaluated as they are likely to be used under field conditions. For example, although the Kjeldahl distillation is recommended for accurate ammonia determinations, the more rapid Nessler method will often be used under field conditions, and should, therefore, be evaluated.

All automated methods as recommended by EPA (1974) for water and wastewater and Technicon (1973) for industrial waste should be evaluated for possible interferences since most tests are based on colorimetric analyses which are generally subject to strong interference by the color and suspended solids present in leachate. Such evaluation is necessary since increasing amounts of leachate samples will be analyzed by automated methods at a future date.

It is recommended that further research should be conducted, including a literature search, to establish correlations between specific constituents and general parameters such as conductivity, absorbance at 400 nm and pH. These three parameters are easy to determine and are, therefore, valuable for monitoring and enforcement purposes as they can be used to screen large numbers of samples. Especially when these parameters exceed a certain value, to be determined by further research, will it be warranted to conduct further and more costly chemical analysis.

It is finally recommended that further research establish the exact nature of the interfering substance. When the interference is caused by a common parameter that is generally included in the measurements such as total solids, chlorides or sulfates, the knowledge of the concentration of the interfering parameter can be used to adjust the calculated concentration of the interfered measurement. This eliminates the need to run time-consuming standard addition curves for the interfered measurement. Research should also indicate ways to reduce these interferences when their exact nature has been established. When it is caused by the color and suspended solids present in leachate, massive lime dosages may be effective in eliminating these specific interferences. The effectiveness of coagulation will have to be evaluated. Other steps such as ion exchange or activated carbon treatment to remove certain interferences, also will have to be studied.

# SECTION 3

# INTRODUCTION

The oldest method of solid waste disposal, that of landfilling, is still the most widely used. This method can have an adverse effect on the environment unless sound engineering principles are used during design, operation and long term maintenance of the solid waste fill. When infiltration of rainwater is not restricted the water will dissolve organic and inorganic substances from the solid waste. The leachate thus generated may move out of the fill into the surrounding soil and subsequently pollute groundwaters or nearby aquifers. In several instances regulatory agencies (State of Illinois, 1973) have therefore required monitoring of the environment to determine the impact of landfilling. To minimize such impact clay layers, asphalt, plastic or rubber liners, are placed at the bottom of the fill prior to the disposal of the solid waste (Anon, 1972) to prevent leachate migration. Leachate treatment facilities are then a necessity and have, therefore, been installed at several landfills (Cressman, 1973; Schoenberger, et al., 1971).

The environmental impact of leachate,dependent on leachate strength, attenuation in surrounding soils, biodegradation and efficiency of leachate treatment, requires the accurate, consistent determination of several water contaminants. It is the purpose of the present study to review the analytical methods to determine contaminants as reported in the literature. The methods compiled and evaluated in this study were generally reported in the literature; additional information was obtained by contacting the principal investigators. Interferences in the chemical analysis due to the complex nature of the leachate as enumerated in the reported studies are listed in this report.

The compilation showed that different methods subject to different interferences are used to determine a certain parameter. For each parameter only that method was evaluated in this laboratory, which was found to have the smallest interference. The laboratory evaluation tested the method for its susceptibility to certain interferences commonly found in leachate. In addition the accuracy of the method was tested. All laboratory analyses were performed using a high strength leachate sample obtained from a recently installed lysimeter filled with milled refuse. Recommendations made in this report, therefore, only apply to leachate of similar strength. No evaluation was made of precision and sensitivity of each method since this was beyond the scope of the work. Realizing the above restrictions, recommendations were made in the present study for the selection of those methods least subject to interference. Further recommendations were made concerning modifications of the selected methods.

# SECTION 4

# SAMPLING PROCEDURES

## 4.1 SAMPLE COLLECTION

### Principle

Leachate can be collected from subsurface soil strata by using wells or piezometers placed in drilled holes. A piezometer is a screen or permeable plastic tip fastened to the end of a pipe or tube, installed in a boring. The annulus above it is sealed so that the water level measurements or water samples obtained from this installation apply only to a restricted area in the bottom part of the boring below the seal in the annulus. A well point is similar to a piezometer except that there is generally no seal in the annulus and therefore measurements or water samples obtained from a well point may reflect conditions over a large vertical interval (Hughes, et al., 1971). In some instances the annulus of a well point is also sealed, but it still reflects conditions over a larger vertical interval as obtained with piezometers. Pore water samples above the groundwater table are collected with suction lysimeters (Apgar and Langmuir, 1971). As leachate permeates through the soil in relatively thin strata of higher permeability, the collection device should be placed at such a depth that it includes such permeable strata.

Leachate collected above ground may appear in springs or at the toe of a solid waste disposal site. Such samples may contain eroded soil and will have reacted with the soil to significantly affect its quality. On such samples a suspended solids determination should be performed. The soil should be removed by sedimentation and not by filtration as the latter method may remove significant quantities of heavy metals and phosphates. Filtration (0.45 μ) should only be used when the suspended solids interfere significantly with the chemical analysis.

Leachate may also reach the surface and enter the surface waters directly through groundwater discharge zones. In such instances an estimate will have to be made of the approximate extent of the dilution.

### Interference

The characteristics of leachate can be effected by the methods and materials used. Apgar and Langmuir (1971) for example obtained their sample from suction lysimeters with an effective pore diameter of 1 μ. Hughes et al. (1971) used predominantly No. 10 brass well screens with an opening larger than 5 mm. Fungaroli (1971) did not use drain pipes but collected leachate through sand and glass beads of increasing size. Most studies, however, do not mention the type of sampling device through which the leachate was collected. One of the studies, for example, only mentioned the soil material used to back fill the leachate collection trenches in which perforated pipe was embedded, but did not specify the openings in the leachate collection pipes.

The effective pore diameter of the material through which the leachate is collected may have an appreciable effect on the concentration of several parameters such as suspended solids, phosphates and heavy metals since precipitates or coatings may be formed near the collection device which may filter out these materials.

The construction of the collection devices should be such that it maintains anaerobic conditions and minimizes entry of air, as this will enhance aerobic degradation of the sample. The material used for the construction of the collection device may also have some effect on the leachate characteristics and should therefore be specified.

The aqueous sample present in the subsurface collection device can be obtained by using a bailer, by applying suction or by pressurizing one of the sampling tubes present in the collection device. The sampling device can have an effect on the outcome of the chemical analysis. A bailer, for example, may primarily remove the upper portions of the liquid in the collection device, while suction or pressure devices may preferentially remove the lower portions containing more suspended solids and heavy metals. Complete mixing of the content of the collection device before sampling is therefore necessary. The sample collection above ground is generally less complicated and can proceed by lowering the sample bottle in the leachate stream. When the stream is very shallow, a small trench may have to be excavated to collect sufficient amount of leachate. After construction of the trench it is necessary to allow settling of the soil particles, which otherwise erroneously increase the suspended solids analysis.

The sample volume to be collected will depend on the permeability of the strata, the permeability of the wall of the collection device, the allowed detection time in the collection device and the number of analysis to be performed.

## Recommendation

It is therefore recommended that site and leachate sampling conditions be specified when results of chemical analysis are presented. Such specifications should include a description of the soil, the construction, depth and characteristics of the sampling device, the effectiveness of the device to maintain anaerobic conditions and the approximate detention time of the leachate in the collection device. The content of the collection device will have to be mixed before withdrawal of the aqueous sample. When the leachate is collected from the surface, the soil conditions should be specified as well as the time that the leachate is exposed to aerobic conditions. Other characteristics that will help to explain the results of the chemical analysis should also be reported.

## 4.2 SAMPLE PRESERVATION, HANDLING AND STORAGE

### Principle

Leachate collected from a recently installed solid waste fill will have a translucent light brown color, but it will turn dark green or black and become turbid immediately after collection due to aerobic exposure and the subsequent oxidation of heavy metals and organics. The odor is very disagreeable and nauseating and is generally due to the presence of free volatile fatty acids such as butyric and valeric acid. Leachate samples collected from an older solid waste fill are generally light brown to light yellow and do not change color directly after sampling, since they are more stabilized and have lower metal concentrations. The odor is not offensive since free volatile fatty acids are generally absent due to active methane fermentation. Collection of leachate samples below the surface at older sites, will result in the liberation of $CO_2$ gas bubbles when the sample is exposed to atmospheric pressures, which will cause a reduction in bicarbonate alkalinity.

Cook (1966) showed that storage of leachate with a COD of 1200 mg/ℓ and a pH of approximately 7.5 in a quart jar capped with aluminum foil and maintained at room temperature caused a 55 percent COD reduction after three weeks with most of the decrease occuring after one week. A leachate sample in extensive contact with the atmosphere prior to sampling showed a 61 percent reduction due to the presence of more adapted aerobic microbial populations.

None of the other studies reported in the literature quantitatively measured the changes of specific contaminants with time of storage, although some studies reported visual changes in the sample. None of the studies evaluated the effectiveness of different preservation techniques.

### Evaluation of sample changes

Several characteristics listed in Standard Methods which are used to characterize the nature of leachate, are subject to changes immediately after sampling. To illustrate the necessity of establishing strict sampling procedures, these parameters have been studied simultaneously as a function of time immediately after the sampling of leachate from a lysimeter located at the University of Illinois. The leachate was collected in a 4ℓ bottle filled to the top. Small samples were withdrawn from the bottle at regular intervals for analysis while the capped sample bottle was stored in the coldroom at 4° C. The parameters that were monitored during this period included Chemical Oxygen Demand (COD), Turbidity, Color (absorbance at 400 nm of the 1:10 diluted sample), pH, Suspended Solids (SS), Oxidation Reduction Potential (ORP) and Conductivity (Figure 1 and 2). The most pronounced changes took place with the SS, ORP, turbidity and color of the sample, which corresponded to a visual change of the sample color from light yellow to dark brown. This is caused by the oxidation of the ferrous iron to ferric hydroxide. The formation of ferric hydroxides contributes to the increase of color, turbidity and SS. The increasing ferric hydroxide content of the SS was reflected by the percent of fixed suspended solids which increased from an initial 18.2 percent to 50.3 percent at the end of the monitoring period. Since some of the "apparent" volatile suspended solids is contributed by the loss of bound water in ferric hydroxide at 550° C, the percent of inorganics in suspended solids at the end of the monitoring period may be higher than 50.3 percent. The oxidation of the organic matter and the iron caused a decrease of the COD by 6.8 percent and the formation of a precipitate. It also causes the conductivity to decrease. Figures 1 and 2 depict results of this study within a 12 day period. Eighty minutes after the first sample was withdrawn from the lysimeter, a second sample was collected. Comparison of the data showed that the sample has a higher initial COD of 31,600 versus 31,000 mg/ℓ, while the turbidity, pH and color were slightly higher in the first sample. The ORP was more negative with the first sample than in the second. The initial suspended solids (SS) were approximately equal in both samples. The final COD in the 2 samples after 13 days of storage time was approximately equal, i.e. 29,000 mg/ℓ for the first sample and 29,071 mg/ℓ for the second sample. The final suspended solids were higher for the second sample. Since a fraction of the COD decrease is contributed by the oxidation of the iron, it is expected that an initial higher COD would result in a higher SS and turbidity after prolonged storage. This was indeed observed. In conclusion, the same results of rapid increase of turbidity, SS and color and stabilization of ORP were confirmed with the second sample.

## Recommendations

Based on these observations it is recommended that several parameters be determined directly after collection of the sample or if this cannot be accomplished the leachate should be collected under anaerobic conditions in a tightly stoppered bottle, refrigerated and analysed for the parameters most susceptible to change directly after arrival in the laboratory. The sample should be stored in a glass bottle for organic analysis as this keeps the sample more anaerobic. For heavy metal analysis the sample is preferably stored in a polyethylene bottle as it prevents adsorption of heavy metals onto the wall of the container. The sequence of parameter analyses should be ORP, color, turbidity, suspended solids, pH and conductivity. Other parameters such as COD and organic N may also change directly after sampling but these changes may be reduced when the sample is acidified. Acidification and storage at 4° C will stop the methane fermentation, the process which is responsible for free volatile fatty acid removal, while it also slows the bacterial acid fermentation of complex organic substrates. Acidification, however, enhances volatization of undissociated fatty acids, precipitates humic-like organics and facilitates hydrolysis and oxidation of complex organics. Relative large quantities of acid are also necessary to lower the pH to about 2, causing substantial dilution of other constituents. Preservation with 40 mg/ℓ $HgCl_2$ is not recommended as it is probably not effective. The mercury will be precipitated under anaerobic conditions as mercury sulfide and lose its bactericidal properties. When results of organic analysis are presented, the time lag between sample collection and analysis should be stated.

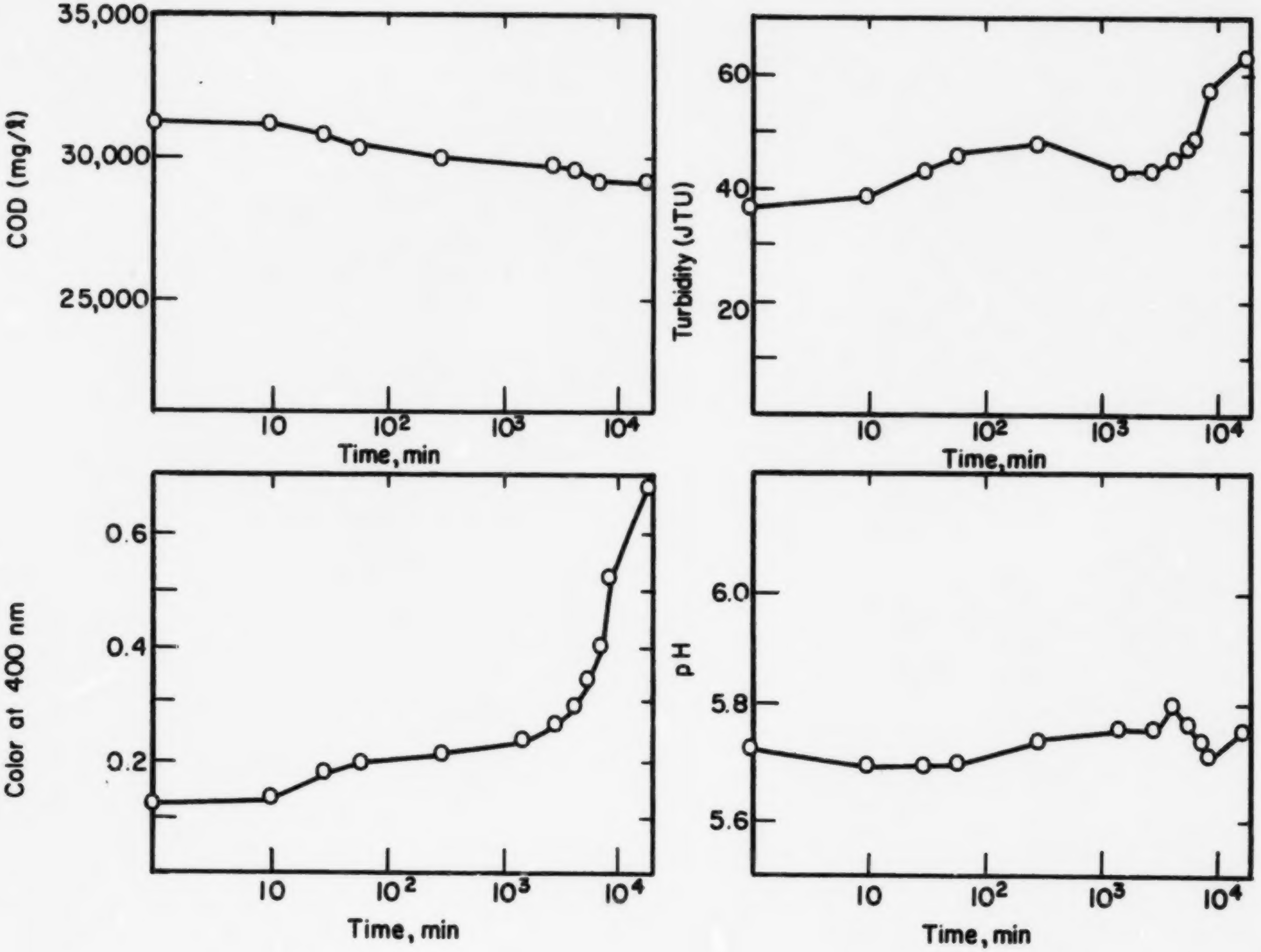

Figure 1. Change of COD, Turbidity, Color and pH with Time of Storage at 4°C

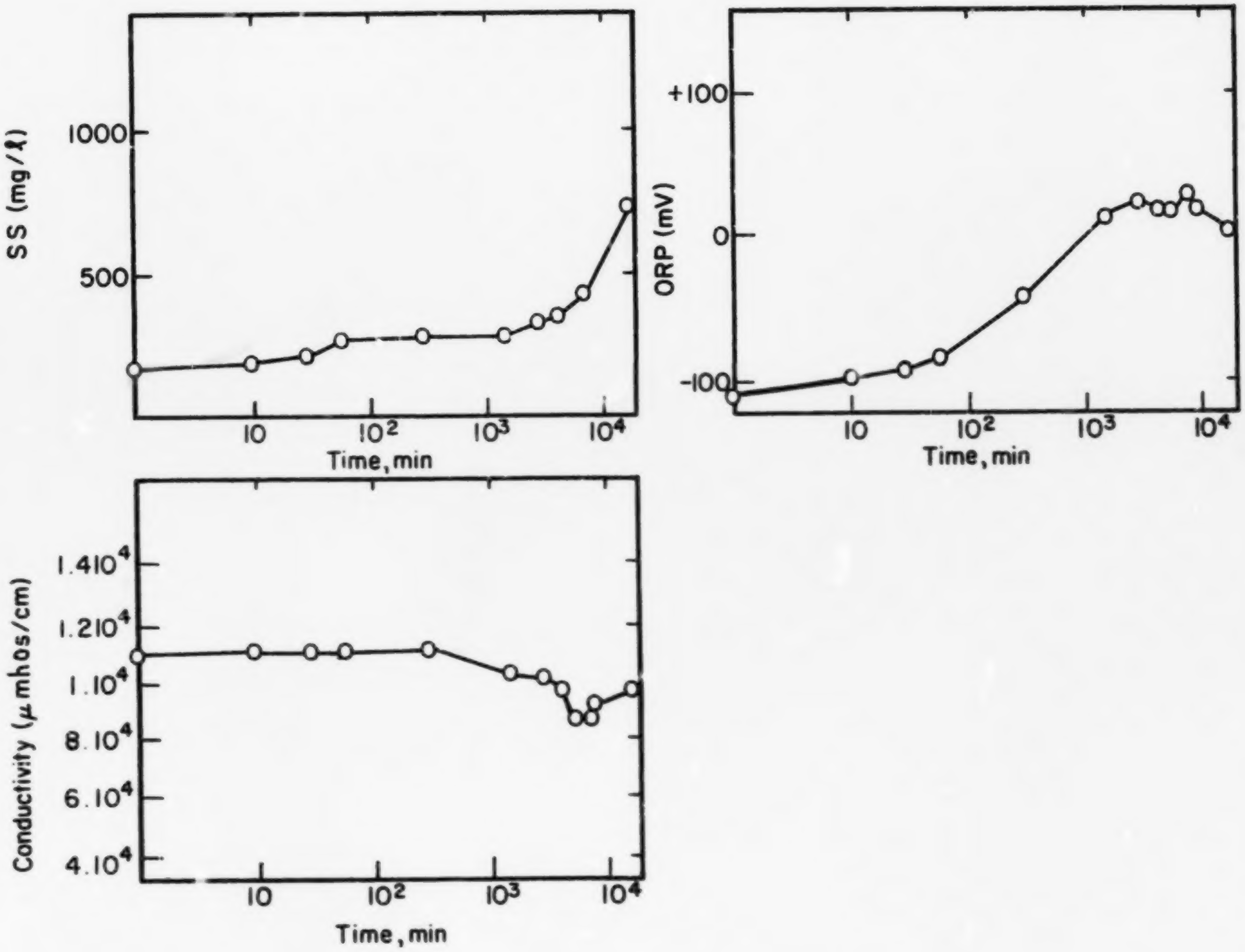

Figure 2. Change of SS, ORP and Conductivity with Time of Storage at 4°C

## 4.3 SELECTION OF PARAMETERS TO BE MEASURED

The remainder of this manual contains numerous analyses that can be performed to characterize the leachate sample. When a large number of samples have to be analyzed it is not feasible to measure all parameters, and those parameters will be determined that are easy to measure. It is felt that most information is obtained by measuring conductivity (attributed by salts and volatile free fatty acids), color or absorbance at 400 nm (attributed by iron and organics) and pH (a low pH indicates presence of volatile free fatty acids). When more parameters are to be measured they should include COD (reflects concentration of organics) and total solids (reflects presence of organics and inorganics). Especially after the above five parameters exceed a certain value is it warranted to determine other parameters such as TOC, free volatile fatty acids, BOD, organic nitrogen or specific anions and cations.

It is recommended that when an organic parameter such as TOC or organic nitrogen is measured, the inorganic equivalent is also included such as the bicarbonate concentration and the ammonia concentration. The ratio organic-C: (organic-C + inorganic-C) then reflects the degree of biological stabilization of the sample, since acid fermentation followed by methane fermentation converts the complex organics to free volatile fatty acids, which are then converted into methane and carbon dioxide. The latter dissolves to a significant degree into the leachate and is reflected in the increased bicarbonate concentration. A high ratio would indicate little organic degradation, while a lower ratio would reflect increasing stabilization. However, it should be realized that the titration method is not applicable for the bicarbonate determination in leachate since free volatile fatty acids are also included. The only accurate way is therefore to measure the inorganic carbon with the duel channel organic carbon analyzer using the inorganic channel.

The ratio organic-N: (organic-N + ammonia-N) does not represent major analytical problems and both measurements can be made sequentially with the Kjeldahl apparatus. The ammonia is first distilled off, whereafter the organic nitrogen is digested, converted to ammonia and subsequently distilled off.

## 4.4 COMPLICATIONS DURING FIELD SAMPLING

The preferred sampling conditions as discussed in the earlier sections may not always exist in certain field situations. Sampling wells may not be present, in which case leachate samples, possibly diluted by groundwater, will have to be collected from an excavated trench at the toe of the fill. If collection devices are present, the aerobic conditions may have resulted in the partial degradation of the organics in the leachate. In such a situation more emphasis will have to be placed on analysis of inorganic parameters such as chlorides and heavy metals. When the sample containers are not refrigerated during handling and storage further degradation will occur. An evaluation in the authors laboratory showed that aerobic conditions and storage at roomtemperature caused a 14% COD decrease in 6 days. Anaerobic conditions at roomtemperature caused a 4% COD decrease, while anaerobic conditions at 4° C caused a 3% decrease. Deviations of the recommended procedures, which may occur because of limitations dictated by field conditions, will affect the outcome of the chemical analysis and should therefore be recorded together with the results of the chemical analysis.

# SECTION 5

## METHODOLOGY OF METHOD EVALUATION

Since most of the leachate studies have been conducted by researchers in the sanitary or environmental engineering fields, the methods that are used closely reflect those of Standard Methods (APHA, 1971). Studies between 1960 and 1965 used the 11th edition, between 1965 and 1971 the 12th edition and after 1971 the 13th edition. Laboratories not employing complicated instruments, sometimes use methods listed by Hach Chemical Company, Handbook of Water Analysis (Hach Chemical Company, 1973). Methods used by geologists are generally those reported in Techniques of Water Resources Investigation of the U. S. Geological Survey (U. S. Geological Survey, 1970). Recent studies use the EPA procedures in Methods for Chemical Analysis of Water and Wastes (EPA, 1974) which also contain optional procedures for automated analysis. Most studies employing automated chemical analysis, however, use methods recommended by Technicon Industrial Systems, Industrial Methods (Technicon, 1973).

The different parameters that have been determined in the studies reported in the literature are listed below. Each section contains a survey of the different methods used to analyze a certain parameter, and the obtained experiences. The method least interferred with by the matrix of the leachate sample was selected and then evaluated in greater detail in the present study. The method was evaluated with the standard addition method and by using progressively increasing dilutions.

### 5.1 STANDARD ADDITION METHOD

The standard addition method is widely used in chemical analysis when interferences present in the sample cannot be avoided. An advantage of this method is that it avoids the necessity of preparing synthetic standards of a composition similar to that of the sample (Geological Survey, 1970). In this method equal volumes of sample are added to a water blank and standards containing increasing but known amounts of the test element. The volume of the blank and the standards must have the same volume to result in a similar dilution of the sample. The diluted samples containing increasing amounts of the test element are then analyzed according to the standard procedures. The obtained values are then plotted on the vertical axis of a graph while the concentration of the known standards are plotted on the horizontal axis (Figure 3). When the resulting line is extrapolated to zero measured concentration, the point of interception of the abscissa is the concentration of the unknown element. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction of the ordinate. Since the scale of the ordinate and abscissa are identical, a line drawn under 45° from the extrapolated point on the abscissa to the ordinate represents a 100 percent recovery of the added element. Thus 100 percent of the known amount added to the diluted sample is recovered. If the actual line connecting the points has a slope lower than 45° the recovery of the added element is less than 100 percent while a slope higher than 45° represents a higher than 100 percent recovery. The

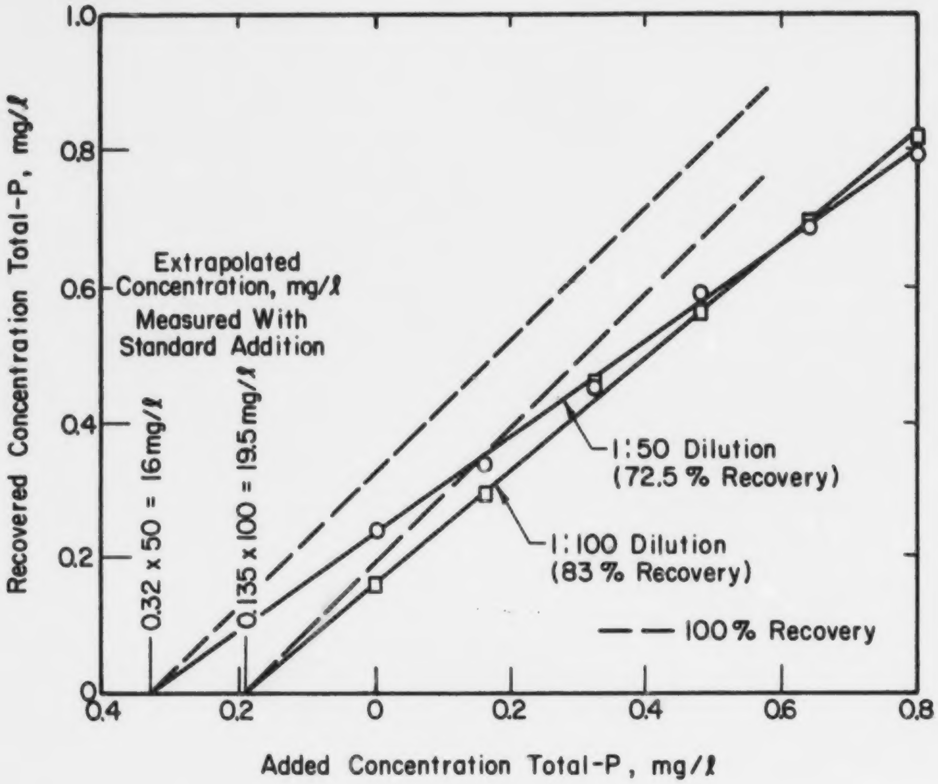

Figure 3. The Total-P Determination with the Ascorbic Acid Method in the 1:50 and 1:100 Diluted Leachate Sample Using the Standard Addition Method

actual percentage recovery can be calculated from the tangent of the line connecting the data points. This is identical to taking the intersect of the ordinate and dividing it by the extrapolated value on the left side of the abscissa.

### 5.2 DILUTION METHOD

In the dilution method the sample is diluted with increasing amounts of distilled deionized water and analyzed according to the standard procedures. The obtained concentration is then adjusted for its dilution effect to give the apparent initial concentration before dilution (Figure 4). The apparent concentration is then plotted vertically and the dilution factor horizontally. The apparent concentration generally increases at increasing dilution till it reaches a plateau value. This indicates that matrix interferences of the sample, which generally result in lower aparent concentrations, are reduced with increasing dilution. The dilution associated with this plateau value are then used to determine the other leachate samples in the batch. At very high dilution the spectrophotometer is not able to record absorbances accurately, resulting in high apparent concentrations in the initial sample. Comparison of the dilution method and the standard addition method as evaluated for the total phosphate determination, showed that the latter is generally more accurate. The former, however, is easier to administer, and requires less time. Both the standard addition method and the dilution method require the analysis of a "sample blank", i.e. the sample in its final dilution containing all the reagents except the color forming reagent. In the heavy metal analysis the sample blank is analysed by measuring the broad non specific absorption at a wavelength bordering the analyte line.

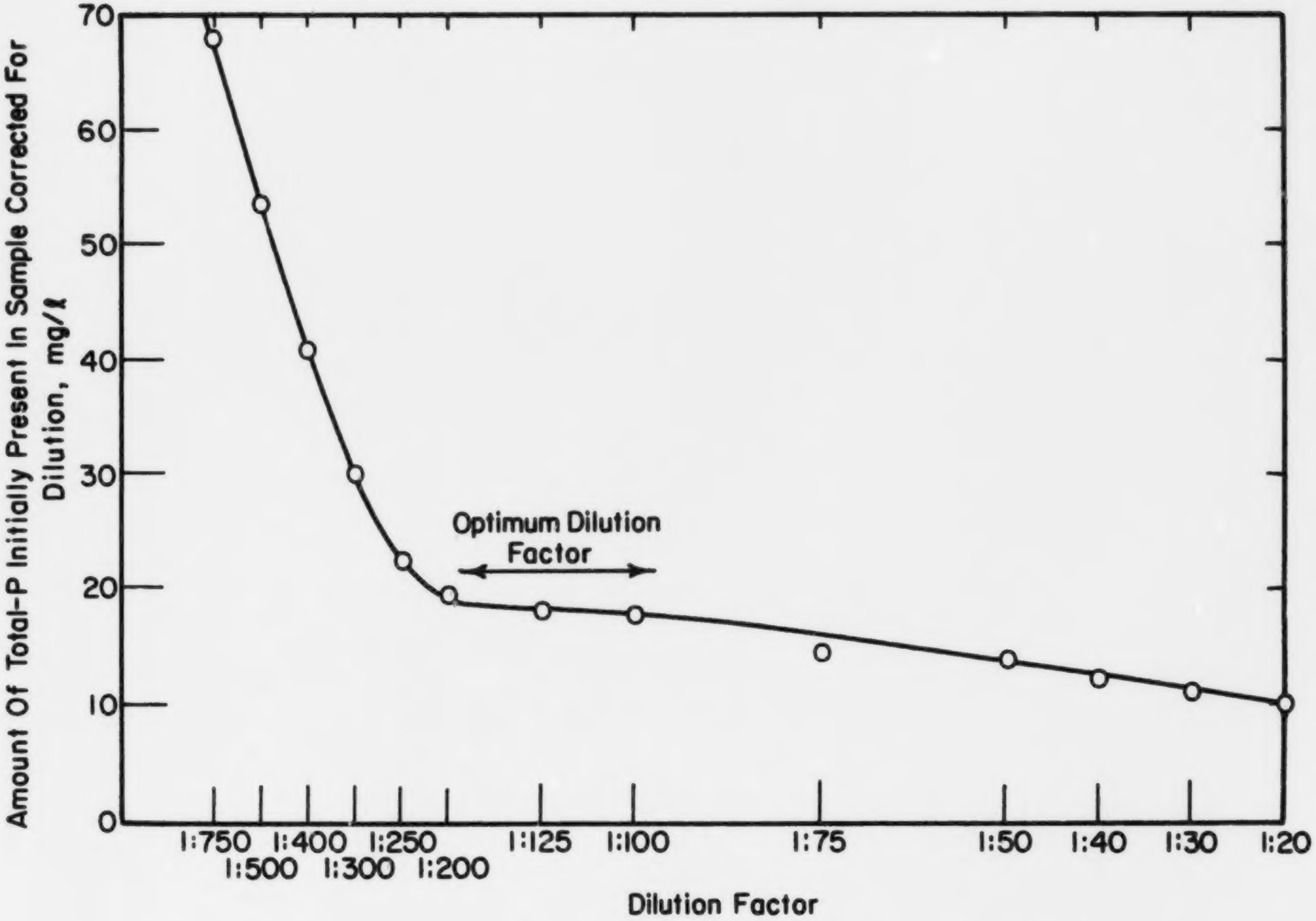

Figure 4. The Total-P Determination with the Ascorbic Acid Method in a Leachate Sample Using the Progressive Dilution Method

# SECTION 6

# PHYSICAL PARAMETERS

This section includes determinations that require physical measurements such as measuring a voltage, a current or a weight. Included in this section are the determinations of pH, ORP, conductivity and residue.

## 6.1 pH DETERMINATION

### Principle

The pH is the logarithm of the reciprocal of the hydrogen activity in moles per liter. The pH of leachate from a fill recently generating leachate will have an acidic pH between 4 and 5 as a result of the predominant presence of free volatile fatty acids. Biologically more stabilized or "older" leachate will have a pH between 5 and 8 as a result of the predominant influence of the bicarbonate buffer system. In those leachate samples the pH may increase directly after sampling as a result of $CO_2$ liberation. All studies evaluated used the electrometric method employing a glass electrode and a calomel reference electrode or a combined electrode (Appendix A). One study used a 10 percent $KNO_3$ Orion reference electrode (Fungaroli, 1971).

### Interference

The glass electrode is relatively immune to interference from color, turbidity, colloidal matter and reducing agents. No significant interference was therefore reported in the studies evaluated.

### Recommendations

It is recommended that the pH be determined electrometrically using a glass electrode and a calomel reference electrode or a combination electrode. A wide selection of commercially available meters are used for recording. The temperature at which the recording is made should be stated.

### Procedures

"Because of the differences between the many makes and models of pH meters which are available commercially, it is impossible to provide detailed instructions for the correct operation of every instrument. In each case, follow the manufacturer's instructions. Thoroughly wet the glass electrode and the calomel electrode and prepare for use in accordance with the instructions given. Standardize the instrument against a buffer solution with a pH approaching that of the sample, and then check the linearity of electrode response against at least one additional buffer of a different pH. The readings with the additional buffers will afford a rough idea of the limits of accuracy to be expected of the instrument and the technic of operation." (Standard Methods, 13th Ed., 1971, p. 279)

## 6.2 ORP DETERMINATION

### Principle

When the activities of dissolved species in a system differ from unity the potential observed at equilibrium is termed the Oxidation Reduction Potential (ORP). Relative oxidizing or aerobic systems generally have positive values while reducing or anaerobic systems generally have a negative value. The ORP can be calculated from the concentration of the redox determining species such as $SO_4^=$ and $S^=$ or $Fe^{3+}$ and $Fe^{2+}$, but is most easily determined by electrometric measurements. The observed potential is that between an inert metal electrode usually platinum and a reference electrode, usually a calomel electrode. Most pH meters can be used for measuring these potentials in which case the glass electrode is replaced by a platinum electrode. The ORP measurement is more meaningful than the dissolved oxygen measurements since most leachate samples have a similar DO value of less than 1 mg/ℓ, while at the same time the ORP will be widely different. For interpretation of redox potentials the pH must be known. Leachate samples in the acid fermentation phase can have an ORP from zero to minus 100 mV. The ORP may decrease to minus 200 mV after the subsequent methane fermentation. The ORP in biologically stabilized leachate can have an ORP of zero to +200 mV (Chian and DeWalle, 1975). Of the surveyed studies six measured this parameter and reported that stable and satisfactory readings could be obtained (Appendix A).

### Interferences

Contamination by coating of the Pt electrode may sometimes occur and may be corrected by boiling the electrode in 1:1 $H_2SO_4$ or by heating it to red hot in a gas flame.

### Recommendations

It is recommended that this parameter be determined electrometrically concurrently with a pH determination.

### Procedures

Samples must be handled with the same precautions as for pH. Connect a Pt electrode to the indicator electrode terminal of the pH meter and switch the range to "millivolts". Most pH meters have a millivolt range from -700 to +700 or from -1000 to +1000. Because of the different models available commercially, it is impossible to provide detailed instructions for the correct operation of each instrument. In each case the manufacturer's instructions should be followed.

## 6.3 CONDUCTIVITY

### Principle

The specific conductance of leachate reflects the total concentration of ionic solutes and is a measure of the capacity to convey an electric current between 2 platinum electrodes each with a surface area of 1 $cm^2$ placed 1 cm apart. In leachate from a fill recently generating leachate, both inorganic and organic species such as free volatile fatty acids contribute to the conductivity. Since the conductivity of acids depends on the degree of dissociation, the conductivity measurement is pH dependent. In older leachate the conductivity is mainly attributed to $Na^+$, $K^+$ and $HCO_3^-$ ions and to a lesser extent to fulvic acids; the measurement becomes, therefore, less pH dependent.

### Interferences

Fouling of the electrode surfaces may occur and checks of the indicated conductance using another cell may be necessary. A chromium-sulfuric acid mixture is effective in cleaning the electrodes. Other solutions as recommended by the manufacturer of the instrument are also satisfactory.

### Previous Studies

Many studies measure this parameter in leachate and report satisfactory results with the measurement. Some studies that limit the number of chemical tests use the conductivity as the most important parameter to identify the migration of leachate in groundwater. The conductivity of biologically stabilized leachate may decrease during seepage through soils as a result of cation exchange in which $Ca^{++}$ and $Mg^{++}$ is replaced by $Na^+$ but may increase as a result of nitrification in which $NH_4^+$ is converted to $NO_3^-$ and $H^+$. Most studies use electrodes with a cell constant of 1. A constant of 0.1 is generally not used since it requires dilution of the sample which will affect the pH and dissociation of several species.

### Recommendations

It is recommended that the conductivity be determined concurrently with the pH employing a commercially available meter and electrode with a cell constant of 1. Both the temperature and pH sould be determined as it effects the results. The results should be reported at the temperature recommended by manufactures, which is generally 25°C.

### Procedures

The instrument must be standardized with a 0.01 m KCl solution before daily use. "Dissolve 745.6 mg anhydrous KCl in freshly boiled double-distilled water and make up to 1,000 ml at 25° C. This is the standard reference solution, which at 25° C has a specific conductance of 1,413 micromhos/cm.

Rinse the conductivity cell in the potassium chloride solution and measure the resistance. Record this value as $R_{KCl}$. Next rinse the cell and measure the resistance of the first samples; proceed in the same way until all the water samples have been measured. Do not measure the resistance of the KCl solution again unless there is a temperature drift of more than a few tenths of a degree during the set of measurements. Repeat the KCl measurement, however, with every subsequent set of water samples.

The cell constant, C, is equal to the product of the measured resistance, in ohms, of the standard potassium chloride solution, and the specific conductance, in mhos per centimeter, of standard solution; $C = R_{KCl} \times 0.001413$ if the measurement is made at 25° C.

The specific conductance (mho/cm) of the water sample at 25°C is equal to the cell constant, C, divided by the resistance, in ohms, of the sample, $R_s$, measured at 25° C:

$$\text{Specific conductance} = \frac{C}{R_s}$$

It is standard practice to express it in micromhos/cm.

If the temperature of measurement is not exactly 25° C, it may be more convenient to calculate the specific conductance at 25° C according to the equation:

$$\text{Specific conductance} = \frac{1.413 \times R_{KCl}}{R_s} \text{ micromhos/cm}$$

where $R_{KCl}$ and $R_s$ are measured at the same temperature, preferably near room temperature, and in the range from 20 to 30° C." (Standard Methods, 13th Ed., 1971, pp. 326-327).

## 6.4 RESIDUE DETERMINATION

### Principle

The residue determination includes the total solids (TS) and volatile solids (VS). A further differentiation is made between the dissolved solids (DS) and suspended solids (SS) also defined as nonfilterable and filterable residues. In both fractions the total and volatile solids can be determined. The total residue is the weight of the solids left after evaporation of the water on a steambath and its subsequent drying to constant weight in an oven at 103-105° C. The volatile solids are calculated from the weight difference between 550° C (for 1 hour) and 105° C. The residue determinations are not subject to the usual criteria of accuracy since many uncontrolled factors can influence the determination. The distinction between dissolved and suspended solids is an operational one since it uses filtration through a filter to differentiate between the two fractions. The filter can be a glass fiber filter, membrane filter or ashless filter paper, and may have a pore size of 0.45 μ to several microns.

### Interferences

The determination of the total solids can vary due to volatilization of part of the organic matter, loss of occluded water and gasses from heat induced chemical decomposition. The suspended solids determination is affected by the physical nature of the material in suspension, the pore size of the filter, and the area and thickness of the mat.

### Previous Studies

Most studies determine the total solids and volatile solids since it is a relatively rapid and simple determination. The general procedure is used of drying the sample to constant weight at 105° C after which it is heated at 550° C for 1 hour. Some studies, however, heat to 580° C or 600° C for 10 minutes to 1 hour (Appendix A). A relatively large number of studies also determine the suspended solids and most use glass fiber filters. Only one study used a membrane filter, while one study used air drying at room temperature (Appendix A).

### Evaluation of Method

The TS test was evaluated to determine the effect of drying the sample at 25° C and 103° C, respectively. Since free volatile fatty acids comprise a large fraction of the organic matter, the higher drying temperature may result in a lower TS reading. In order to verify this, leachate samples, initially stored in the coldroom (5° C), were dried at 25° C and at 103° C, respectively and than stored in the disiccator before weighing. Thereafter, the dried residues were redissolved and analyzed for COD. The results of these measurements are reported in Table 1 which shows clearly that drying at 103° C reduces the TS reading as can be seen by the ratio of $TS_{103}/TS_{25}$ of 0.808. A ratio of 1 would indicate no effect of drying temperature on TS. The COD of the redissolved sample showed a much smaller influence of the drying temperature. The ratio of $COD_{103}/COD_{25}$ was found to be 0.98.

It was also evaluated whether aerobic degradation of the sample would influence the above results. The data show that the $TS_{103}/TS_{25}$ ratio is somewhat higher with the aerated sample, i.e. a value of 0.818 versus 0.808 as obtained with the unaerated sample stored at 5° C. However, the

|  | TS (25°C) (mg/l) | TS (103°C) (mg/l) | $TS_{103}/TS_{25}$ | COD (25°C) of redissolved sample (mg/l) | COD (103°C) of redissolved sample (mg/l) | $COD_{103}/COD_{25}$ |
|---|---|---|---|---|---|---|
| 1. Leachate sample (stored at 5°C) | 23,320 | 18,840 | 0.808 | 30,800 | 30,200 | 0.98 |
| 2. Leachate sample aerated for 14 days | 17,860 | 14,610 | 0.818 | 28,200 | 25,400 | 0.936 |
| 3. Supernatant of centrifuged aerated leachate sample | 8,280 | 6,060 | 0.732 | 8,400 | 6,800 | 0.810 |
| 4. Precipitate of centrifuged aerated leachate sample | 10,068 | 8,950 | 0.892 | 19,356 | 19,200 | 0.992 |
| 5. 3 + 4 added | 18,348 | 15,010 | 0.819 | 27,756 | 26,000 | 0.937 |

Table 1. Effect of Drying Temperature on the Total Solids (TS) Determination

ratio of $COD_{103}/COD_{25}$ is lower with the aerated sample. The aerated leachate sample was then separated into two fractions using a centrifuge to determine whether the change of these ratios was due to the suspended solids or dissolved solids. Table 1 shows that both TS and COD ratios are lower for the soluble fractions as compared to the suspended solids fraction. The increase in the $TS_{103}/TS_{25}$ in the aerated leachate, as compared to the leachate sample stored in the cold room, is therefore the result of the increased suspended solids, since the $TS_{103}/TS_{25}$ ratio of the suspended solids is higher than the dissolved solids. A decrease of the COD ratio of the aerated sample as compared to the stored leachate sample appears to be due to a change in the soluble organics, and a relatively higher concentration of the more volatile lower molecular weight free volatile fatty acids such as acetic acids which are expected to be found in the aerated sample as a result of microbial degradation of the higher molecular weight fatty acids such as valeric and caproic acid in leachate. The above data show that TS is best determined at 103° C, since a substantial amount of bound water will be removed at this temperature with only 2 percent of the organics volatilized as compared to 25° C. However, after the sample is aerobically degraded, the loss of volatile matter may reach as high as 6 percent with comparable amounts of the bound water removed when the drying process is conducted at 103° C, as compared to 25° C.

The volatile solids (VS), representing the weight loss between 103° C and 550° C, were evaluated in a similar fashion as the TS test. Figure 5 shows that when the temperature was increased from 550° C to 650° C the VS value increased by 8 percent. The additional loss of weight above a temperature of 550° C is attributable to the volatilization of inorganics such as carbonates, since no more removal of COD was observed. Results of temperature study on volatile solids measurements for leachate support procedures outlined by Standard Methods which suggests a furnace temperature of 550° C for VS determination.

## Recommendations

It is recommended that the total solids be determined after drying to constant weight at 105° C while the volatile solids are determined from the weight loss at 550° C for one hour. The suspended solids are best determined using a glass fiber filter and selecting similar temperatures as for the total solids. A glass fiber filter is preferred since it is able to filter a leachate sample in the presence of a high concentration of suspended solids.

## Procedure for Total Solids

"Subject the dish to be used in the determination of total residue to a preliminary drying in an oven at the same temperature intended for the residue. If ignition of the residue is to be carried out for determination of fixed total residue, ignite the dish in a furnace for 30 min at 550° C.

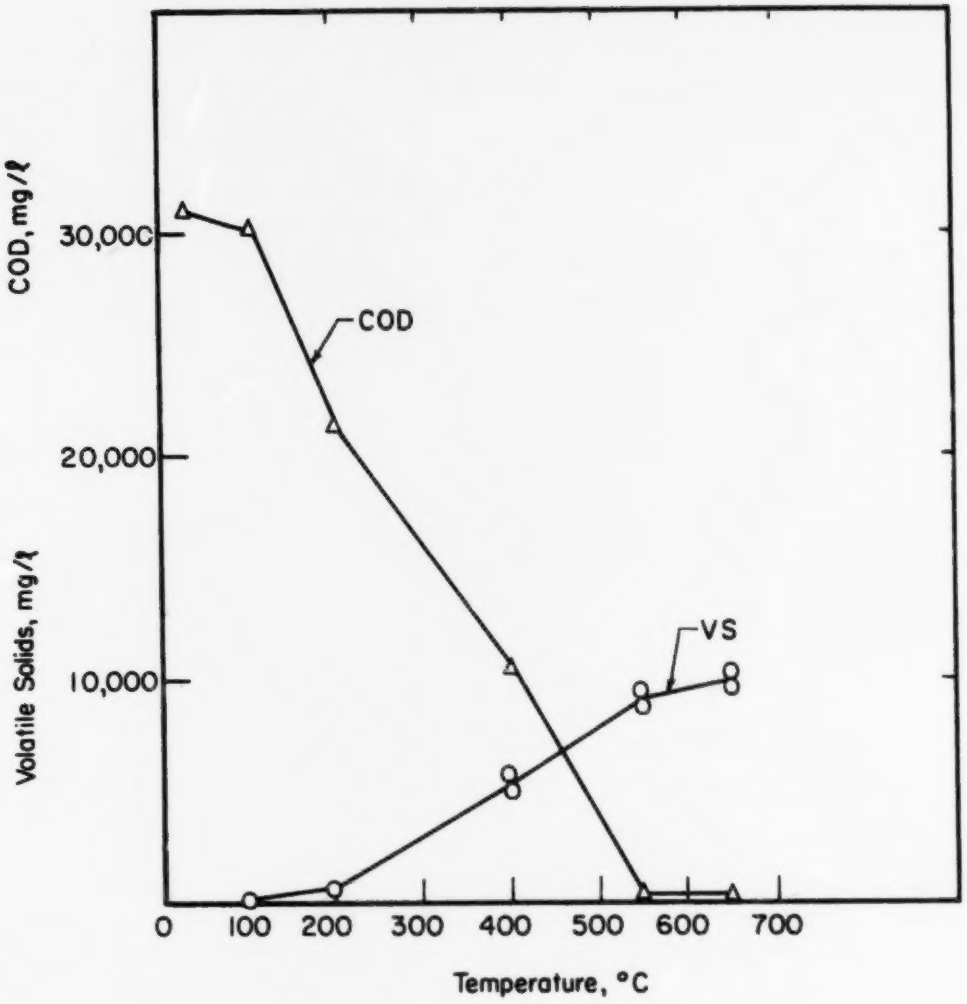

Figure 5. Effect of Heating Temperature on the Volatile Solids Determination when Sample was Heated for One Hour in a Furnace

Choose a volume of sample which will yield a residue between 25 and 250 mg, and preferably between 100 and 250 mg. Estimate the volume to be evaporated from the specific conductance value.

Pour a measured portion of the well-mixed sample into a weighed evaporating dish on a steam bath. After complete evaporation of the water from the residue, transfer the dish to an oven maintained at 103-105° C. Dry to constant weight. Consider constant weight to be attained when not more than a 0.5 mg weight change occurs between two successive series of operations consisting of heating, cooling in a desiccator, and weighing.

Allow the dish to cool briefly in air before placing it, while still warm, in a desiccator to complete cooling in a dry atmosphere. Do not overload the desiccator. Provide sufficient room so that all dishes may remain flat on the desiccator shelf, and no part of a dish touches another dish or the side of the desiccator.

Weigh the dish as soon as it has completely cooled. Do not allow the residue to remain overly long in a desiccator because some residues are very hygroscopic and may remove water from a desiccant that is not thoroughly dry. Report the increase in weight over the empty dish as 'total residue' on drying at 103° C in terms of mg/ℓ and to the nearest whole number. For results exceeding 1,000 mg/ℓ report only three significant figures."

$$\text{mg}/\ell \text{ total residue} = \frac{\text{mg total residue} \times 1{,}000}{\text{m}\ell \text{ sample}}$$

(Standard Methods, 13th Ed., 1971, p. 289).

### 6.7 Procedure for Fixed or Volatile Residue

"Take the residue produced in 6.4 and ignite in the dish or filter in a muffle furnace at a temperature of 550° C for 1 hr in order to insure reproducibility. Have the furnace up to temperature before inserting the sample.

After ignition, allow the vessels to partially cool in air until most of the heat has dissipated, then transfer to a desiccator for final cooling in a dry atmosphere. Do not overload the desiccator. Weigh the vessel as soon as it has completely cooled. Report the increase in weight over the empty ignited vessel as 'fixed total residue', in terms of mg/ℓ and to the nearest whole number. For results exceeding 1,000 mg/ℓ report only three significant figures.

$$\text{mg}/\ell \text{ fixed residue} = \frac{\text{mg fixed residue} \times 1{,}000}{\text{m}\ell \text{ sample}}$$

(Standard Methods, 13th Ed., 1971, p. 292-293).

### Procedure for Filtrable Residue

If the determination is to be made directly by weighing the residue, subject the filter to a preliminary drying an oven at the same temperature intended for the sample. Consider 2.5 mg as the minimum amount of residue to be significant in direct weighing.

"After filtration transfer the filter with its contents to an oven maintained at a temperature of 103-105° C and dry until constant weight is attained. Cool briefly in air and transfer to a desiccator to complete the cooling in a dry atmosphere. Report the increase in weight over that of the empty filter as 'nonfiltrable residue' on drying at 103° C in terms of mg/ℓ and to the nearest whole number. Also report the type of filter used.

$$\text{mg}/\ell \text{ nonfiltrable residue} = \frac{A \times 1{,}000}{\text{m}\ell \text{ sample}}$$

where A = mg 'nonfiltrable residue'. (Standard Methods, 13th Ed., 1971, p. 292).

# SECTION 7

# ORGANIC CHEMICAL PARAMETERS

Since the objectionable nature of leachate from a recently generating landfill is caused to a large extent by the dissolved organics such as free volatile fatty acids, it is important to analyze for these parameters. In biologically more stabilized leachate the organic matter concentration is generally low and does not contribute significantly to any odor. The organics in such samples will only contribute to the color of the sample.

## 7.1 THE COD DETERMINATION

### Principle

The chemical oxygen demand (COD) indicates the quantity of oxidizable materials that are present in a water sample and is expressed as the oxygen equivalent of the organic matter that is susceptible to oxidation by a strong chemical oxidant. A relation exists between COD, TOC and BOD depending on strength of the leachate and age of the landfill since all three parameters measure certain aspects of the organic matter. Ratios of BOD to COD values may be as high as 0.8 for leachate from a recently generating fill while it may decrease to less than 0.1 for biologically stabilized leachates. Similarly the COD/TOC ratio may decrease from 3.5 to less than 1 indicating progressing oxidation of the organic matter. These ratios are subject to considerable variation due to the nature of the solid waste and climatic conditions.

### Interferences

Straight chain aliphatic compounds and acids are not oxidized to an appreciable extent, but addition of $Ag_2SO_4$ will increase the oxidation. When relatively large quantities are added to the sample, $HgSO_4$ will have to be added first, to complex the high chloride concentrations as a soluble mercuric chloride complex as the choride would otherwise have reacted with the silver.

### Previous Studies

Most studies determine the COD according to procedures outlined in Standard Methods. The addition of sulfonic acid is generally omitted since nitrite is generally not present in high concentrations as compared to the organic substances. $HgSO_4$ is sometimes added in larger quantities than the 0.4 g/20 ml sample as specified in Standard Methods due to the high chloride content of the sample. Fungaroli (1971) reduced the quantity of strong sulfuric acid added to the sample from 30 ml to 15 ml. Ott (1974) increased the dichromate concentration from 0.25 N to 0.5 N and used a shorter reflux time to reduce the time necessary to run the test. Although the COD value is generally higher than the BOD, Hughes et al. (1971) noted on several occasions that the BOD value was larger than the COD. This, however, was the result of the longer incubation time of the BOD test which was 20 days as opposed to 5 days as recommended by Standard Methods.

### Evaluation of the Method

The COD test was evaluated by varying four parameters, i.e., the amount of dichromate added, the concentration of sulfuric acid used, reflux time and the procedure of acid addition. Figure 6 shows that increasing the amount of sulfuric acid beyond the 30 ml recommended by Standard Methods increases the COD value by 7 percent. This increase is larger, i.e. 18 percent when the concentration of dichromate is doubled. However, it is not recommended to use the larger amount of sulfuric acid since the condensate which drops down into the heated sample in the flask, does not mix very well with the sample, and will have a tendency of blowing the content out of the flask. Increasing the normality of the dichromate is also not recommended since lower COD values are obtained (Figure 6) due to the higher decompositions of the dichromate. Also, a larger error will be introduced due to the high normality of the dichromate. Results of the reflux time show that most of the organics are oxidized within the first 30 minutes of refluxing (Figure 7) indicating that the reflux time recommended by Standard Methods is satisfactory. The effectiveness of the reflux time was also evaluated by determining the TOC in the COD flask after refluxing. Assuming that most of the organics were present as acetic acid, it was calculated that 4.8 percent of the COD was not oxidized. This indicates that a fraction of the organic matter was highly resistant to oxidation.

The COD test was evaluated with respect to the procedure of acid addition. The 13th edition of Standard Methods specifically recommends addition of the acid through the condenser, while such a requirement was not mentioned in the previous editions. Since most leachate studies in the past followed the earlier editions, it was important to evaluate this aspect. Duplicate tests showed that the COD of the sample to which the acid was added through the condenser was 1.48 percent higher than that of the sample to which the acid was added directly to the Erlenmeyer flask containing the 1:20 diluted leachate sample.

Separate experiments were conducted to substantiate the result of the above findings. A small scrubber containing 5 ml of NaOH was used to collect the fumes that evolved from the leachate sample. The scrubber connected to the COD flask, to which the acid was added directly, contained a TOC of 36.1 mg/l. Using a COD/TOC ratio of 2.67 for acetic acid, it was calculated that 3.98 percent of the COD finally measured in the sample was lost through volatilization. The TOC of the scrubbing solution connected to the COD apparatus was found to be 11.2 mg/l when acid was added through the reflux condenser. This represents a COD loss of 2.28 percent of the COD finally measured. On the basis of a material balance using TOC data obtained from the scrubber, the value of the COD should be 1.70 percent higher with the acid addition through the condenser. However, on the basis of the actually measured COD values, the difference was found to be 1.48 percent as reported above, indicating some discrepancy of the two measurements.

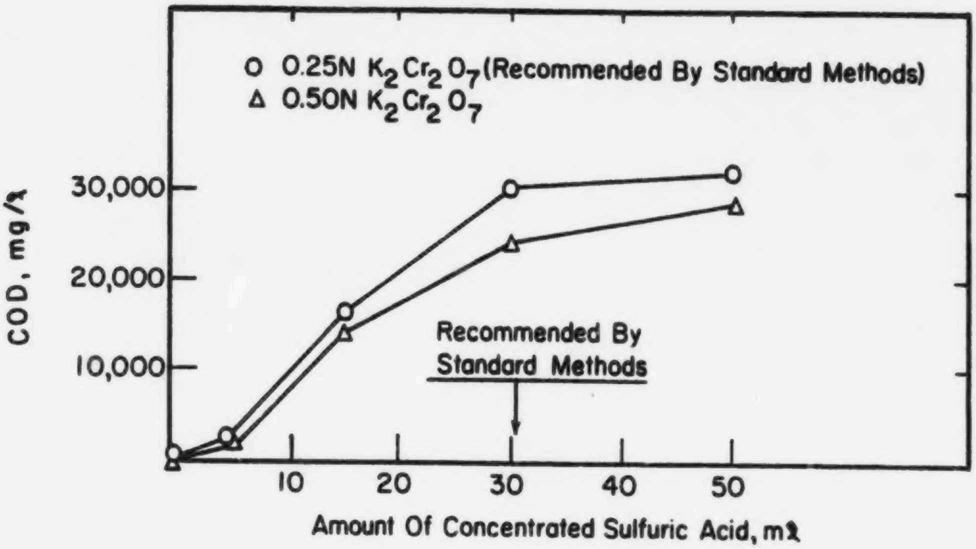

Figure 6. Effect of Amount of Sulfuric Acid and Normality of Dichromate on the Results of the COD Test

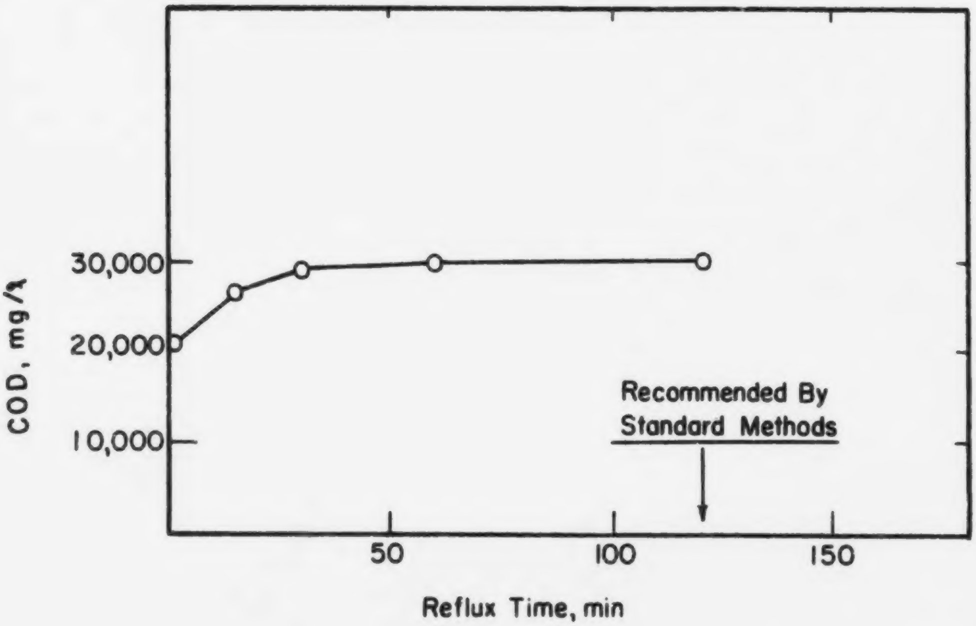

Figure 7. Effect of Reflux Time on the Results of the COD Test

For some of the leachate samples analyzed in this lab, the test was conducted by adding acid and dichromate long before the samples are refluxed. This time lag before refluxing on COD values was thus evaluated. Results of this study show that when the time lag between reagent addition and refluxing is one day, the final COD value decreases by an additional 0.6 percent. This additional COD loss increases to 1.9 percent after a period of 3 days between reagent addition and reflux.

It can therefore be concluded that the most important variables in the COD test are the amount of acid added and that of dichromate used. The procedure of acid addition and the time lag between reagent addition and reflux are less important variables in the COD test. The precision of the COD test was determined with five replicate samples containing 1000 mg/ℓ lactose solution. A mean of 1058.2 mg/ℓ COD and a standard error of 6.7 mg/ℓ, or 0.63 percent were found in this study. Therefore, the reported variations of COD data are generally within the accuracy of the COD test. The study showed that a minimum of 30 mℓ of concentrated sulfuric acid should be used with 0.25 N potassium dichromate. The use of 15 mℓ of concentrated sulfuric acid as opposed to 30 mℓ may decrease values by as much as 46 percent. Using a higher dichromate concentration and shorter reflux time may decrease values by as much as 30 percent. The Technicon Autoanalyzer may result in slightly lower COD values since the refluxing takes place for only 25 minutes as compared to 120 minutes while the quantity of $AgSO_4$ catalyst is only 60 percent of that recommended by Standard Methods. However, this may have been counteracted by the higher reflux temperature of 145° C and the higher sulfuric acid content which is 10 times higher than recommended by Standard Methods. Chlorides may interfere in the autoanalyzer determination since the quantity of $HgSO_4$ is only 2.5 percent of that recommended by Standard Methods.

### Recommendations

It is recommended that the COD method be executed as outlined in Standard Methods by using 30 mℓ concentrated sulfuric acid and 0.25 n potassium dichromate. In the few instances that the COD is less than 100 mg/ℓ more accurate results are obtained by using the low level COD in which all reagents are diluted ten times.

### Reagents

"Standard potassium dichromate solution, 0.250N: Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103° C for 2 hr, in distilled water and dilute to 1,000 mℓ.

Sulfuric acid reagent, conc. $H_2SO_4$ containing 22 g silver sulfate, $Ag_2SO_4$ per 9-lb bottle (1 to 2 days required for dissolution).

Standard ferrous ammonium sulfate titrant, analytical-grade crystals, 0.10N: Dissolve 39 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 mℓ conc. $H_2SO_4$, cool, and dilute to 1,000 mℓ. This solution must be standardized against the standard potassium dichromate solution daily.

Standardization - Dilute 10.0 mℓ standard potassium dichromate solution to about 100 mℓ. Add 30 mℓ conc. $H_2SO_4$ and allow to cool. Titrate with the ferrous ammonium sulfate titrant, using 2 or 3 drops (0.10 - 0.15 mℓ) ferroin indicator.

$$\text{Normality} = \frac{m\ell\ K_2Cr_2O_7 \times 0.25}{m\ell\ Fe(NH_4)_2(SO_4)_2}$$

Ferroin indicator solution: Dissolve 1.485 g 1,10-phenanthroline-monohydrate, together with 695 mg $FeSO_4 \cdot 7H_2O$ in water and dilute to 100 mℓ. This indicator solution may be purchased already prepared.*

Silver sulfate, reagent powder (see para. above).

Mercuric sulfate, analytical-grade crystals." (Standard Methods, 13th Ed., 1971, pp. 496-497).

## Procedures

"Place 0.4 g $HgSO_4$† in a refluxing flask. Add 20.0 mℓ sample, or an aliquot diluted to 20.0 mℓ with distilled water, and mix. Then add 10.0 mℓ standard potassium dichromate solution and several pumice granules or glass beads which have been previously heated to 600°C for 1 hr. Connect the flask to the condenser. Slowly add 30 mℓ conc. $H_2SO_4$ containing $Ag_2SO_4$ through the open end of the condenser, mixing thoroughly by swirling while adding the acid. Mix the reflux mixture thoroughly before heat is applied; if this is not done, local heating occurs in the bottom of the flask, and the mixture may be blown out of the condenser.

Use 0.4 g $HgSO_4$, to complex 40 mg chloride ion, or 2,000 mg/ℓ when 20 mℓ of sample are used. If more chloride is present, add more $HgSO_4$ to maintain a $HgSO_4$:Cl ratio of 10:1. If a slight precipitate develops, it does not adversely affect the determination.

Reflux the mixture for 2 hrs. or use a shorter period for particular wastes if it has been found to give the maximum COD. Cool and then wash down the condenser with distilled water.

---

[*] G. F. Smith Chemical Company, Columbus, Ohio.

[†] $HgSO_4$ may be measured conveniently by volume, using a reagent spoon (e.g. Hach Company No. 638 or equivalent).

Dilute the mixture to about 150 $m\ell$ with distilled water, cool to room temperature, and titrate the excess dichromate with standard ferrous ammonium sulfate, using ferroin indicator. Generally, use 2-3 drops (0.10-0.15 $m\ell$) of indicator. Although the quantity of ferroin is not critical, do not vary it among samples even when analyzed at different times. Take as the end point the sharp color change from blue-green to reddish brown, even though the blue-green may appear within minutes.

Reflux in the same manner a blank consisting of 20 $m\ell$ distilled water, together with the reagents.

$$mg/\ell \text{ COD} = \frac{(a - b)N \times 8{,}000}{m\ell \text{ sample}}$$

where COD = chemical oxygen demand from dichromate, a = $m\ell$ $Fe(NH_4)_2(SO_4)_2$ used for blank, b = $m\ell$ $Fe(NH_4)_2(SO_4)_2$ used for sample, and N = normality of $Fe(NH_4)_2(SO_4)_2$." (Standard Methods, 13th Ed., 1971, p. 497, 498, 499).

## 7.2 THE TOC DETERMINATION

### Principle

A small wastewater sample is vaporized and then oxidized to $CO_2$ in a furnace at 950° C. A carrier stream of pure oxygen removes the $CO_2$ from the furnace and leads it into an infrared analyzer to provide a measure of the $CO_2$. To distinguish between organic and inorganic carbon a separate sample is heated at 150° C to remove the inorganic carbon in a carrier stream of pure oxygen which is then determined in an infrared analyzer. Subtraction of the two measurements provide the value for the total organic carbon (TOC). Relations have been established between TOC, COD and BOD. Based on theoretical considerations the COD/TOC cannot exceed 4 while it may decrease to one for strongly oxygenated and biologically stabilized leachate samples.

### Interference

This procedure is only applicable to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter syringe. The needle opening of the syringe limits the maximum size of particles which may be included in the sample. Lower TOC values are also obtained when some volatile organics are stripped from the sample and oxidized during the inorganic carbon determination at a temperature of 150° C.

### Previous Studies

Several studies use the TOC measurements (Appendix A) in conjunction with COD to provide a measure of the amount of organic matter present in leachate. Acidification of the sample is sometimes warranted to dissolve the suspended ferric hydroxide solids that otherwise would clog the syringe opening and is also used to preserve the sample.

### Evaluation of the Method

The TOC test is a method having fewer complications than the COD test to determine the amount of organic matter present in leachate samples. Great care, however, should be taken to get the TOC analyzer in optimum working condition. If this requirement is not met, the results of TOC analysis will not be reliable. Procedures developed in this study allow the adjustment of the TOC Analyzer to a condition which allows the TOC measurement within the 10 mg/ℓ range with good accuracy and reproducibility (Figure 8). The maximum error is within ± 1 mg/ℓ which is in good agreement with that claimed by the manufacturer. The background TOC of the dilution water, a doubly distilled deionized water, is shown by the intercept at the ordinate (∿ 4 mg/ℓ) which agrees well with the values between 3-4 mg/ℓ TOC determined in many instances in this laboratory. The background TOC of the dilution water should be subtracted from both the standard solutions and the diluted leachate samples. This correction for background TOC of the dilution water has not been emphasized in the latest edition of Standard Methods (1971).

Loss of accuracy of TOC analysis in the presence of high concentrations of dissolved solids was evaluated by making a TOC mass balance on a leachate sample obtained from a recently generating solids waste landfill. The centrifuged sample was fractionated with a 10,000 MW ultrafiltration membrane. The results of analysis are shown in Figure 9. Figure 9 shows that it is necessary to correct for the distilled water TOC since the standard and the leachate sample are made up with distilled water. Figure 9 also shows that the variation of the recorder height is slightly more pronounced for the 10,000 MW UF retentate sample than for the permeate due to the relatively high iron content in the former fraction. However, the reproducibility of both fractions is very good due to the high dilution used, which will effectively eliminate any interference. The inorganic channel generally shows a better reproducibility than the total carbon channel because it is not interfered by the presence of suspended solids.

Calculation of the actual TOC concentrations showed that inorganic carbon contribution was negligible as compared to the organic carbon in the sample analyzed. The mass balance is then made by taking into account the concentration effect of the UF membrane and the dilution of the permeate by the washing of the retentate with distilled water. The result shows that the adjusted TOC of the fractions comes within 99.9 percent of

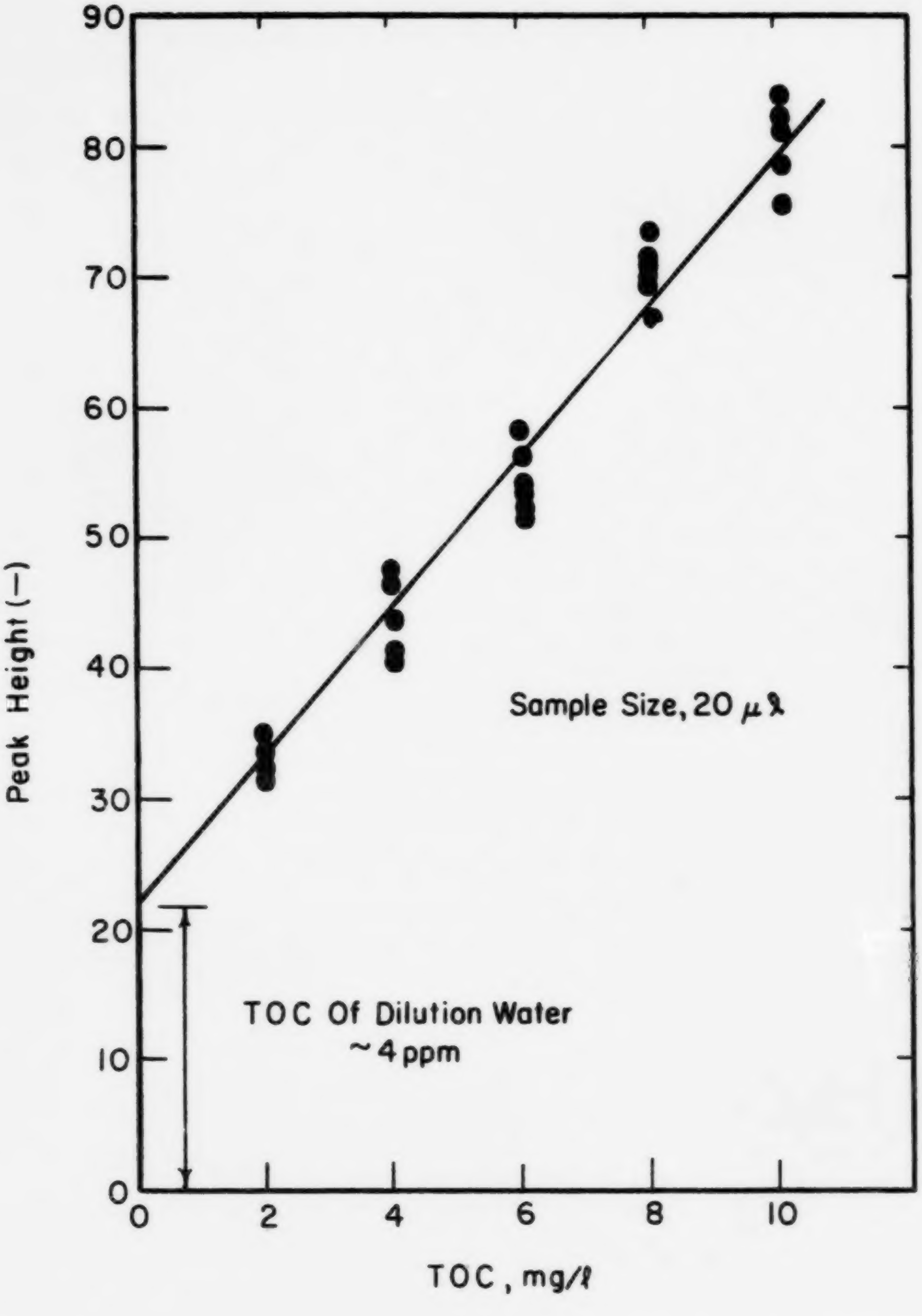

Figure 8. Calibration Curve of TOC Analyzer for Low Concentration Ranges

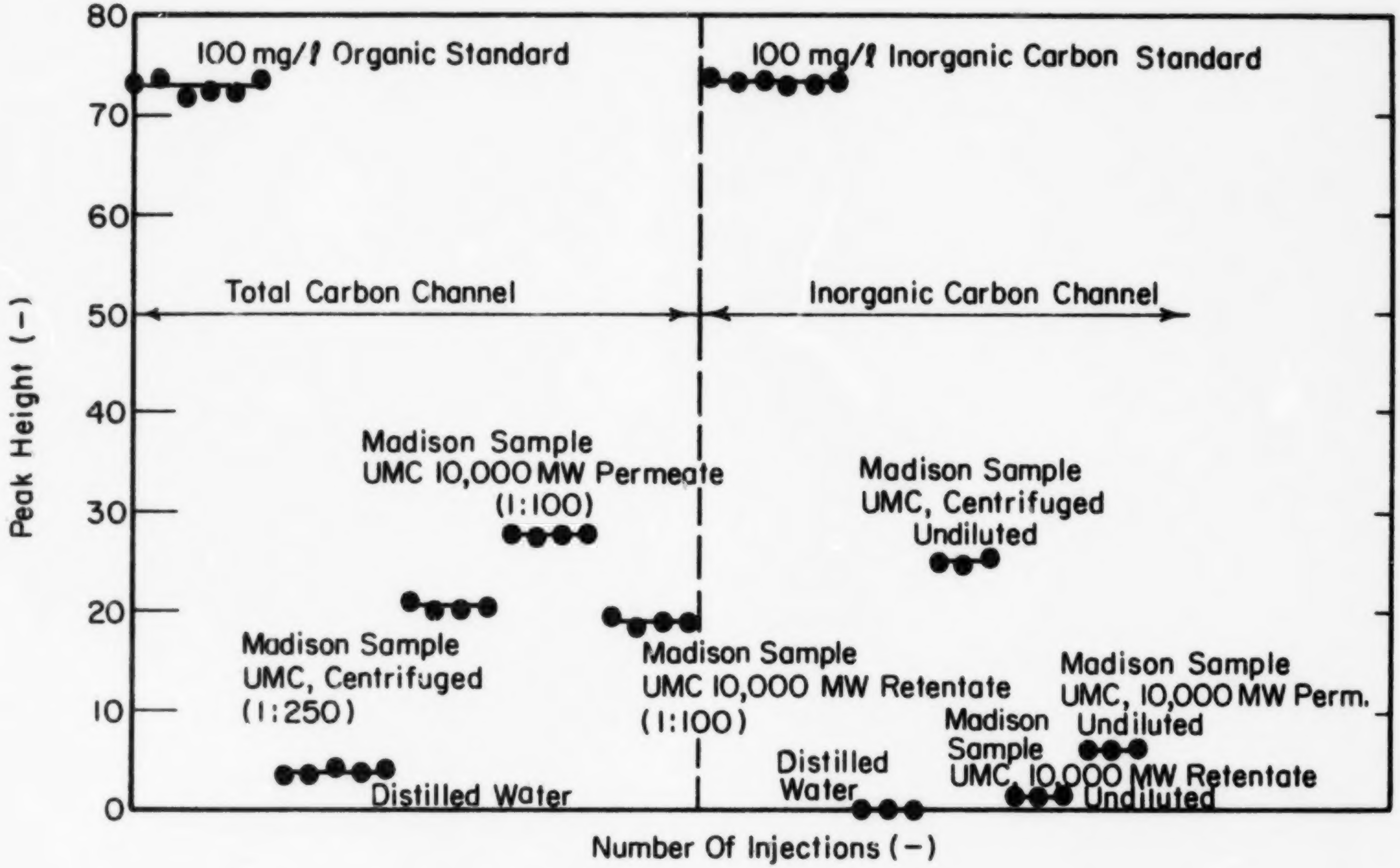

Figure 9. The TOC Analysis of a Membrane Fractionated Leachate Sample Obtained from an Unmilled Covered Landfill (UMC)

the TOC of the original leachate sample, confirming the reliability of this test. The above results show that the TOC test is an accurate method if a sufficiently high dilution of the leachate sample is made to neutralize interfering suspended solids. The results have to be corrected for any TOC contributed by the dilution water.

## Recommendation

The TOC analysis should be determined according to Standard Methods. When the analysis is run on samples diluted with distilled water, the TOC contribution of the distilled water should be taken into account.

## Procedures

Instrument operation: The differences between satisfactory analyzers render impossible the formulation of detailed instructions applicable to every instrument. Therefore, follow the manufacturer's instructions for assembly, testing, calibration and operation of the analyzer on hand. Vary the injected sample size from the normally recommended 20μl to 100-200 μl when an enlarged combustion tube is available.

Sample treatment: When the sample contains suspended solids contributed by iron hydroxide, acidify the sample to disperse the solids. When the sample contains soil particles filter the sample through a glass fiber filter and determine the suspended solids concurrently.

Preparation of standard curve: Prepare a standard carbon series of 10, 20, 30, 40, 50, 60, 80 and 100 mg/ℓ with redistilled water by diluting 10, 20, 30, 40 and 50 mℓ standard carbon solution to 1,000 mℓ, and 30, 40 and 50 mℓ standard carbon solution to 500 mℓ. Inject and record the peak heights of these standards.

Plot the carbon concentrations of the standards in mg/ℓ versus the corrected peak height in millimeters on rectangular coordinate paper. Ascertain the sample concentrations from the corrected peak heights of the samples by reference to this calibration curve.

Calculate the corrected peak height in millimeters by deducting the blank correction in the standards and samples as follows:

$$\text{Corrected peak height in mm} = A - B$$

where A = peak height in mm of the standards or sample, and B, peak height in mm of the blank.

Apply the appropriate dilution factor when necessary.

## 7.3 VOLATILE ACIDS DETERMINATION

### Principle

The 12th and 13th editions of Standard Methods recommend the column partition chromatographic method to determine free volatile fatty acids in water samples. This method has superseded earlier distillation and direct titration methods. An acidified water sample is adsorbed on a column of inert granular material after which the organic acids are extracted from the column with chloroform-butanol solvent, which is then titrated with NaOH.

The volatile acid test is a very important test for leachate since free volatile fatty acids such as acetic and butyric acid comprise the majority of the organics present in a leachate sample obtained from a recently generating landfill. Since this organic fraction can be removed by anaerobic or aerobic bacteria, the organic acid test is a measure of the biodegradability of leachate and as such may be a more accurate test than the BOD. In biologically stabilized leachate samples volatile acids are generally not detected while the sample still may have a considerable COD or TOC or color.

### Interferences

The Standard Methods recommend the tentative Column Partition Chromatographic Method for determining free volatile fatty acids. The only interferences are caused by other organic acids, such as pyruvic, α-ketoglutaric and succinic acids as they adsorb to silicic acid and are eluted off with the butanol-chloroform mixture together with the other free volatile fatty acids. These acids may be present in leachate, judging from the relatively high concentration of carbonyl groups in the 500 MW UF permeate. These compounds are excreted as intermediates and are eventually removed by further biological degradation of leachate.

The other method for fatty acid analysis that has been used is the hydroxylamine test. In this test, acid is esterified with alcohol, the alcohol group is displaced by the hydroxylamine which then gives a colored complex with ferric iron. Since any carboxyl group will respond to such reaction, carboxyl groups from the refractory humic and fulvic acids will contribute to the final reading. This interfering effect becomes more noticeable when the concentration of these refractory organics is relatively large with respect to the fatty acid concentration, which occurs in biologically stabilized leachate. Hughes et al. (1971), for example, found relatively high concentrations of carboxyl groups in old leachates with respect to the COD. Since the $BOD_5$ values were relatively low in these samples with respect to the COD, little or no biodegradable fatty acids would be expected, indicating that in such instances nonfatty acid carboxyl groups are measured.

## Previous Studies

Most studies use the column partition chromatographic method for analysis of organic acids and satisfactory results have generally been obtained when the test is executed with sufficient care (Appendix B). One study used both steam distillation and gas liquid chromatography but no comparisons were given. One study used the gas liquid chromatograph for organic acid analysis. Two studies used the hydroxylamine test to determine the presence of carboxyl groups.

## Evaluation of the Method

The results of analysis with the column partition chromatographic method and the hydroxylamine test with a polluted leachate sample having an initial COD of 31,200 mg/ℓ showed that relatively high concentrations of fatty acids were present (Figures 10 and 11). Comparison of extrapolated results obtained with these two methods showed that the column partition method gave a 4.76 percent higher fatty acid concentration than the hydroxylamine test in the 1:20 diluted sample, while it was 27.8 percent higher in the 1:40 diluted sample. The latter test had the highest percentage recovery (85.7 percent versus 74 percent with column partition method in the 1:20 dilution) when standard amounts of acetic acid were added to the diluted sample. Section 5.1 explains the details of the standard addition method.

The Standard Methods reported a more than 95 percent recovery efficiency for fatty acid concentrations in excess of 200 mg/ℓ as determined with the column partition method. The low recoveries obtained with leachate samples i.e. 74 percent and 61 percent in the 1:20 and 1:40 diluted sample, respectively, therefore indicates the presence of interfering substances. It also means that the test has to be run with standard amounts of fatty acids added to the sample, in order to determine the percentage recovery. Evaluation of Figure 10 also shows that decreasing the dilution from 1:40 to 1:20 increases the percentage recovery but decreases the calculated concentration of fatty acids from 18,400 mg/ℓ to 17,600 mg/ℓ obtained in the 1:40 and 1:20 dilution, respectively. These results therefore indicate that the sample should be diluted as little as possible to increase the percentage recovery as long as the measured concentrations are below 5000 mg/ℓ.

The hydroxylamine test, similar to the column partition method, showed the highest calculated concentration corresponding with the lowest recovery. However, since the discrepancy between the two methods is smallest for the least diluted leachate sample, the hydroxylamine test should be run on the least diluted sample, as long as the concentration is below 5000 mg/ℓ.

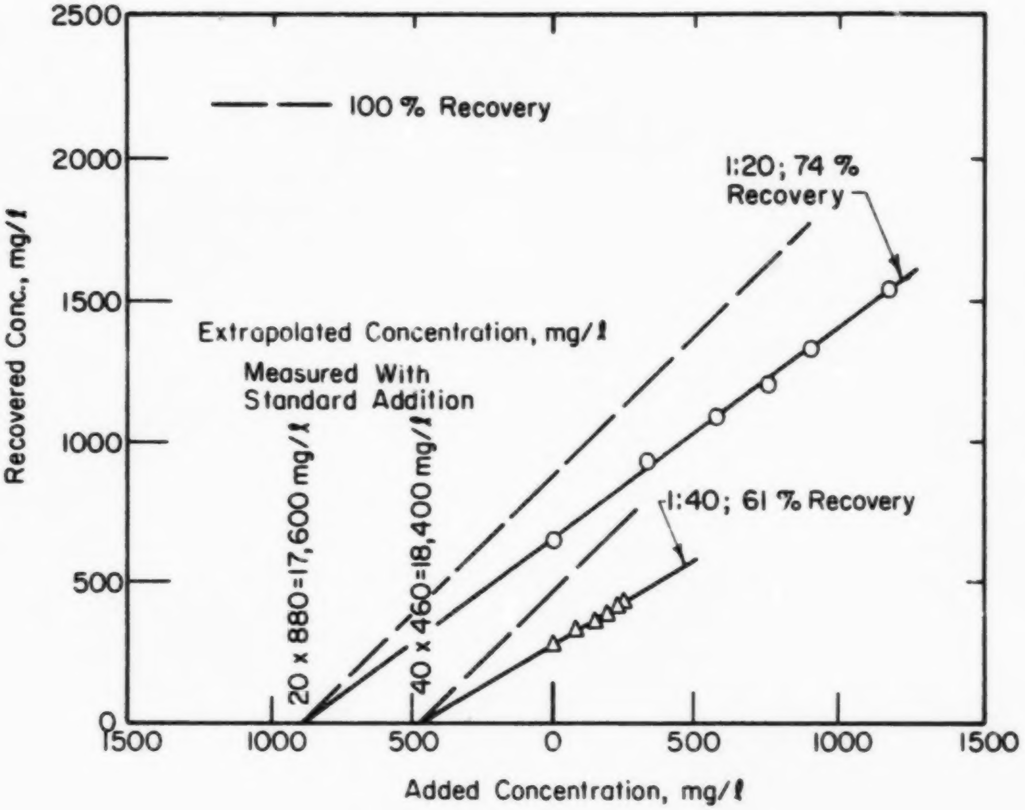

Figure 10. The Organic Acid Determination with the Column Partition Chromatographic Method

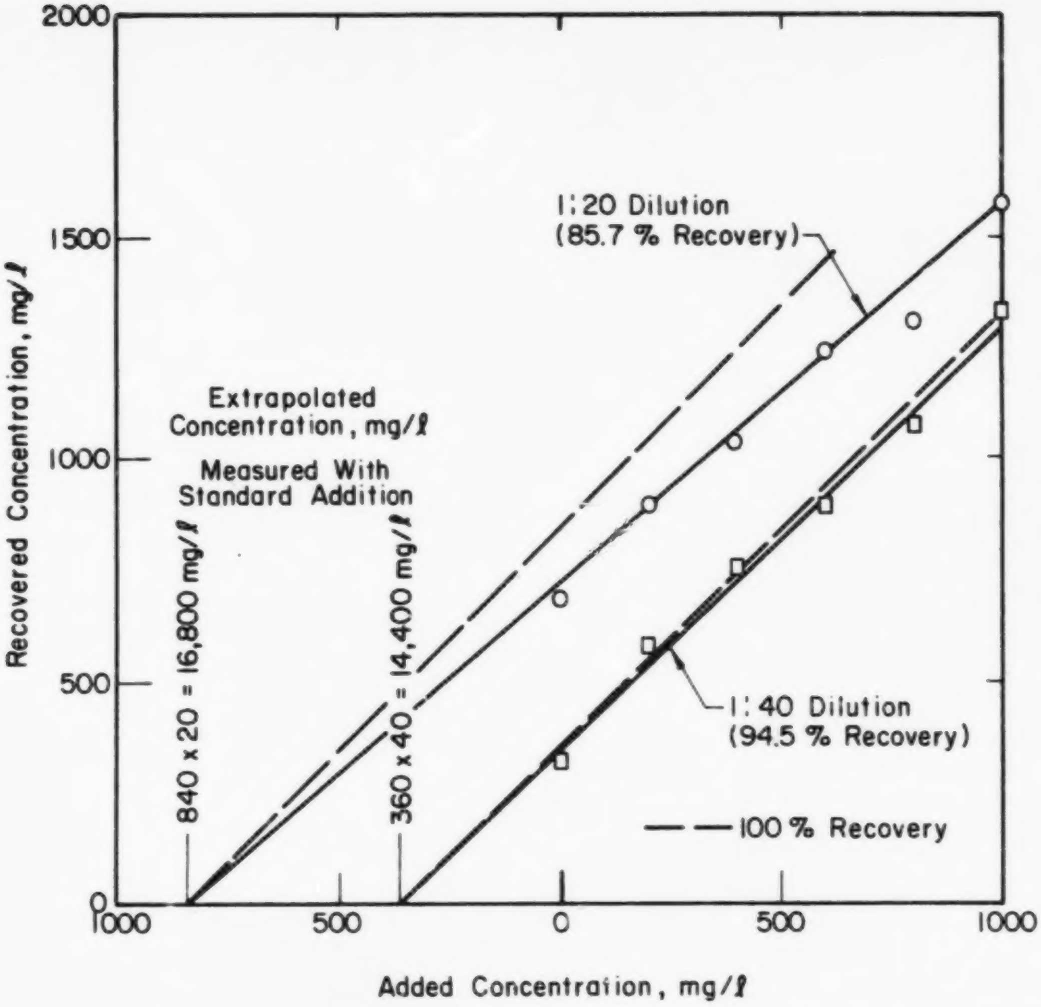

Figure 11. The Organic Acid Determination with the Hydroxylamine Test

## Recommendations

It is recommended that the volatile organic acids be determined with the column partition chromatographic method as listed in Standard Methods and that standard amounts of acid be added to determine the recovery of the method. When the recovery of the added amount is less than 100 percent the obtained values will have to be adjusted using the recovery factor as outlined in Section 5.1.

## Reagents

"Silicic acid, specially prepared for chromatography, 50-200 mesh: Remove fines by slurrying the acid in distilled water and decanting the supernatant after settling for 15 min. Repeat the process several times. Dry the washed acid in an oven at 103° C until absolutely dry, then store in a desiccator prior to use.

Chloroform-butanol reagent, $CB_{25}$: Mix 300 mℓ reagent-grade chloroform, 100 mℓ n-butanol, and 80 mℓ 0.5 N $H_2SO_4$ in a separatory funnel and allow the water and organic layers to separate. Drain off the lower organic $CB_{25}$ layer through a fluted filter paper into a dry bottle.

Thymol blue indicator solution: Dissolve 80 mg thymol blue in 100 mℓ absolute methanol.

Phenolphthalein indicator solution: Dissolve 80 mg phenolphthalein in 100 mℓ absolute methanol.

Sulfuric acid: Conc., reagent-grade $H_2SO_4$.

Standard sodium hydroxide titrant, 0.02 N: Dilute 20 mℓ 1.0 N NaOH stock solution to 1 liter with absolute methanol. Standardize the solution against 0.0200N potassium biphthalate solution which has been prepared by dissolving 4.085 g anhydrous $KHC_8H_4O_4$, and diluting to the mark of a 1-liter volumetric flask with $CO_2$-free distilled water." (Standard Methods, 13th Ed., 1971, pp. 578-579; p. 51)

## Procedure

"Centrifuge enough leachate to obtain 10-15 mℓ clear sample in a small test tube or beaker. Add a few drops of thymol blue indicator solution, then conc. $H_2SO_4$, dropwise until definite color change from red to thymol blue (pH = 1.0-1.2).

Column chromatography: Place 12 g silicic acid in a Gooch or fritted-glass crucible and apply suction to pack the column. With a pipet, distribute 5.0 mℓ of the acidified sample as uniformly as possible over the surface of the column. Apply suction momentarily to draw the sample into the silicic acid, releasing the vacuum as soon as the last portion of the sample has entered the column. Quickly add 65 mℓ $CB_{25}$ reagent to the column and apply suction. Discontinue the suction just before the last of the reagent enters the column. Use a new column for each sample to be analyzed.

Titration: Remove the filter flask and purge the eluted sample with nitrogen gas or $CO_2$-free air immediately before titration.

Titrate the sample with standard 0.02 N NaOH reagent to the phenolphthalein end point, taking care to avoid aeration of the sample. Nitrogen gas or $CO_2$-free air delivered through a small glass tube may be used to purge and mix the sample and to prevent contact with atmospheric $CO_2$ during titration.

Blank: Prepare a blank composed of 5.0 mℓ acidified ($H_2SO_4$) distilled water, place on column, extract with 65 mℓ of $CB_{25}$ reagent, and titrate in a similar manner.

$$\text{Total organic acids (mg/}\ell\text{ as acetic acid)} = \frac{(a-b) \times N \times 60{,}000}{m\ell\ \text{sample}}$$

where a = mℓ of NaOH titrant used for sample, b = mℓ of NaOH titrant used for blank, and N = normality of NaOH titrant." (Standard Methods, 13th Ed., 1971, p. 579).

## 7.4 THE TANNIN AND LIGNIN DETERMINATION

### Principle

Aromatic hydroxyl groups are oxidized and reduce tungstophosphoric and molybdophosphoric acid to form a blue color which is measured at 700 nm. The color reaction is similar to that of the phosphate determination and is also able to detect very low concentrations. The test reflects the presence of refractory organics in biologically stabilized leachate and its relative contribution to the organic matter in leachate increases with age of the landfill.

### Interferences

Other easily oxidizable substances such as reduced metal ions, sulfides and nitrite may give a similar reaction in this test and caution should therefore be exercised in evaluating the results. The largest interference is caused by ferrous iron and 2 mg/ℓ will give a color equivalent of 1 mg/ℓ tannic acid.

### Previous Studies

One study used the tyrosine-Hach method to measure aromatic hydroxyls in leachate and generally reported a relative increase parallel to the stabilization of the refuse. Another study reported satisfactory results with the tannin lignin test.

### Evaluation of the Method

An evaluation of the method was conducted by Chian and DeWalle (1975) which showed that the color is best measured at 620 as compared to 700 nm. The intensity of the colored product depends on whether the OH group is in the ortho, meta or para position. When the aromatic ring has three OH groups, one of the groups may not participate in the reaction.

### Recommendations

It is recommended that this test be measured according to Standard Methods.

### Reagents

"Tannin-lignin reagent: dissolve 100 g sodium tungstate dihydrate, $Na_2\text{-}WO_4 \cdot 2H_2O$, 20 g molybdophosphoric acid (also called phosphomolybdic acid), $20MoO_3 \cdot 2H_3PO_4 \cdot 48H_2O$, and 50 mℓ 85 percent phosphoric acid, $H_3PO_4$, in 750 mℓ distilled water. Boil the liquid under reflux for 2 hr; cool and make up to 1 liter with distilled water.

Sodium carbonate solution: dissolve 200 g $Na_2CO_3$ in 500 mℓ warm distilled water and dilute to 1 liter to form a saturated solution. Keep in a rubber-stoppered bottle.

Stock solution: weigh 1.000 g of the tannic acid. Dissolve in distilled water and dilute to 1,000 mℓ.

Standard solution: dilute 10.00 mℓ of 50.00 mℓ stock solution to 1,000 mℓ with distilled water to form a solution containing 10.0 μg or 50.0 μg active ingredient per 1.00 mℓ." (Standard Methods, 3rd Ed., 1971, p. 347).

### Procedure

"Add 2 mℓ tannin-lignin reagent to 50.0 mℓ of clear sample and mix well. After 5 min add 10 mℓ sodium carbonate solution and mix thoroughly. Wait 10 min for color development. Make photometric readings against a reagent blank prepared at the same time. Use the following guide for the instrumental measurements at the wavelength of 620 nm:

| Tannic Acid in 62-mℓ Final Volume µg | Lignin in 62-mℓ Final Volume µg | Light Path cm |
|---|---|---|
| 50-600 | 100-1,500 | 1 |
| 10-150 | 30- 400 | 5 |

(Standard Methods, 13th Ed., 1971, p. 347).

## 7.5 THE ORGANIC NITROGEN DETERMINATION

### Principle

In the presence of sulfuric acid, potassium sulfate and mercuric sulfate catalyst, the amino nitrogen of many organic materials is converted to ammonium sulfate, after which the ammonia is distilled under alkaline conditions by the addition of sodium hydroxide and sodium bisulfite and collected in a boric acid solution. While the Standard Methods (1971) recommend addition of 50 mℓ digestion reagent to 300 mℓ sample, EPA (1971) recommend 100 mℓ digestion reagent for 500 mℓ of sample. Both recommend digestion till $SO_3$ fumes are given off and the solution turns pale yellow. In the automated procedure the sample is digested with the same reagents as used in the Kjeldahl method whereafter the ammonia concentration is determined with the phenate method measuring the blue indophenol color.

### Interferences

The only interferences that are encountered may be due to the incomplete oxidation of the organic nitrogen to ammonia.

### Previous Studies

Most studies selected the Kjeldahl method with digestion, distillation and titration of the ammonia collected in the borate solution with no major difficulties being reported. Only two studies measured the organic nitrogen with the automated procedure, (Appendix A and B).

### Evaluation of the Method

The evaluation of the organic nitrogen test (Figure 12) showed nearly 100 percent recovery with low concentrations of bovine albumin added to the sample. This high recovery is the result of the high buffer concentration which does not cause any pH decrease during the distillation, and the low ammonia concentration present after digestion of the organic nitrogen.

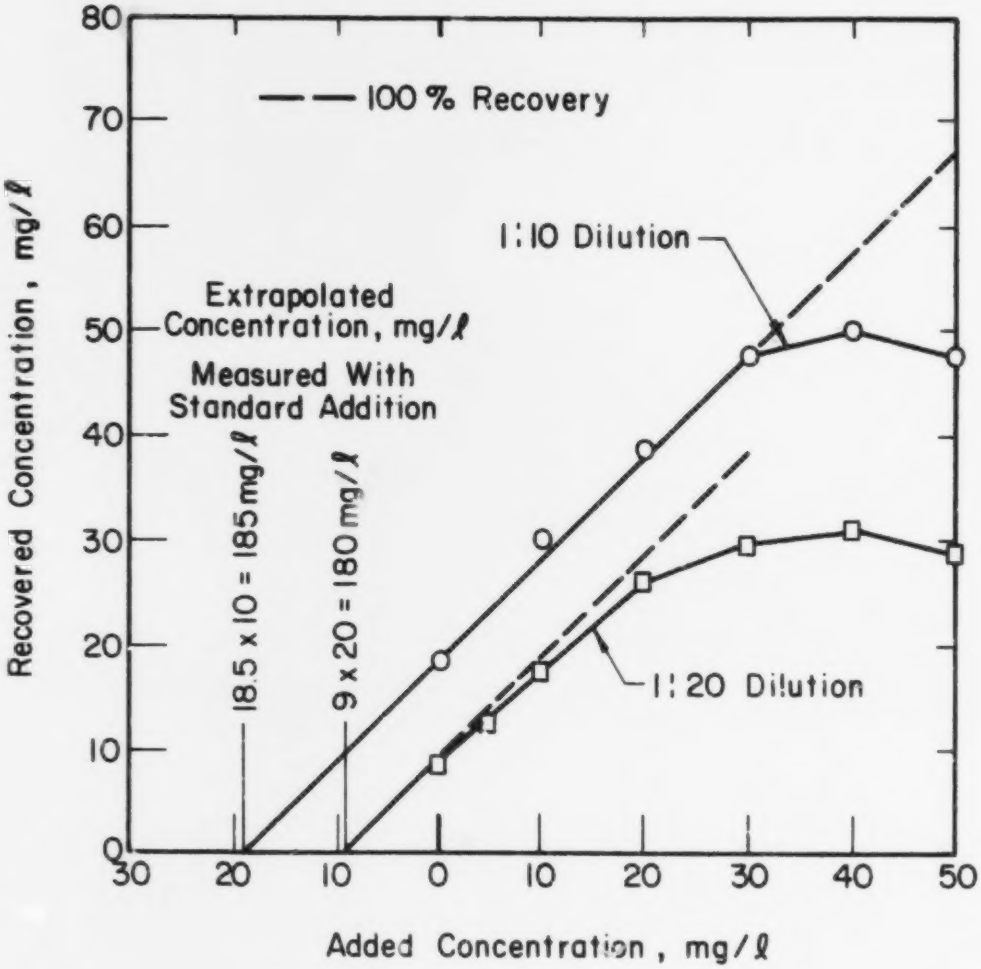

Figure 12. The Organic Nitrogen Determination with the Kjeldahl Method

At higher concentrations of the standard additions, however, the recovery decreases progressively. This is probably due to a pyrolytic charring of the sample which then forms black insoluble humin products that enmesh organic nitrogen present in the sample. The charring was not noticeable at the low additions but became more pronounced at higher concentrations, indicating that the Kjeldahl test may not be able to detect the organic nitrogen at concentrations above 30 to 50 mg/ℓ depending on the dilutions used. However, at the concentrations encountered in leachate from the UI lysimeter and at the dilutions employed no interferences were noted. The charring was found to increase with increasing amounts of digestive reagent used. When the amount of digestive reagent was increased from 50 to 75 and 100 mℓ respectively, the organic-N concentration in the 1:10 dilution decreased from 18.2 to 18.1 and 16.7 mg/ℓ, respectively. Therefore, 50 mℓ digestion reagent was selected as the amount that still gave satisfactory results. Since the duration of the digestion as outlined in Standard Methods is inconclusive an evaluation of the digestion time showed that a period of 30 minutes (after the start of the boiling) is satisfactory since it results in the highest concentration (Figure 13).

### Recommendations

It is recommended that the organic notrogen be determined with the Kjeldahl method as outlined in Standard Methods with 50 mℓ digestion reagent added to 300 mℓ sample while digesting for 30 minutes.

### Reagents

All the reagents listed for the determination of the ammonia nitrogen are required, plus digesting reagent: Dissolve 134 g potassium sulfate, $K_2SO_4$ in 650 mℓ ammonia-free distilled water and 200 mℓ conc. $H_2SO_4$. Add, with stirring, a solution prepared by dissolving 2 g red mercuric oxide, HgO, in 25 mℓ 6N $H_2SO_4$. Dilute the combined solution to 1 liter. Keep this solution at a temperature above 14° C to prevent crystallization.

Phenolphthalein indicator solution.

Sodium hydroxide-sodium thiosulfate reagent: dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_2O$ in ammonia-free distilled water and dilute to 1 liter.

Mixed indicator solution: dissolve 200 mg methyl red indicator in 100 mℓ 95 percent ethyl or isopropyl alcohol. Dissolve 100 mg methylene blue in 50 mℓ 95 percent ethyl or isopropyl alcohol. Combine the two solutions. Prepare monthly.

Indicating boric acid solution: dissolve 20 g $H_3BO_3$ in ammonia-free distilled water, add 10 mℓ mixed indicator solution, and dilute to 1 liter. Prepare monthly.

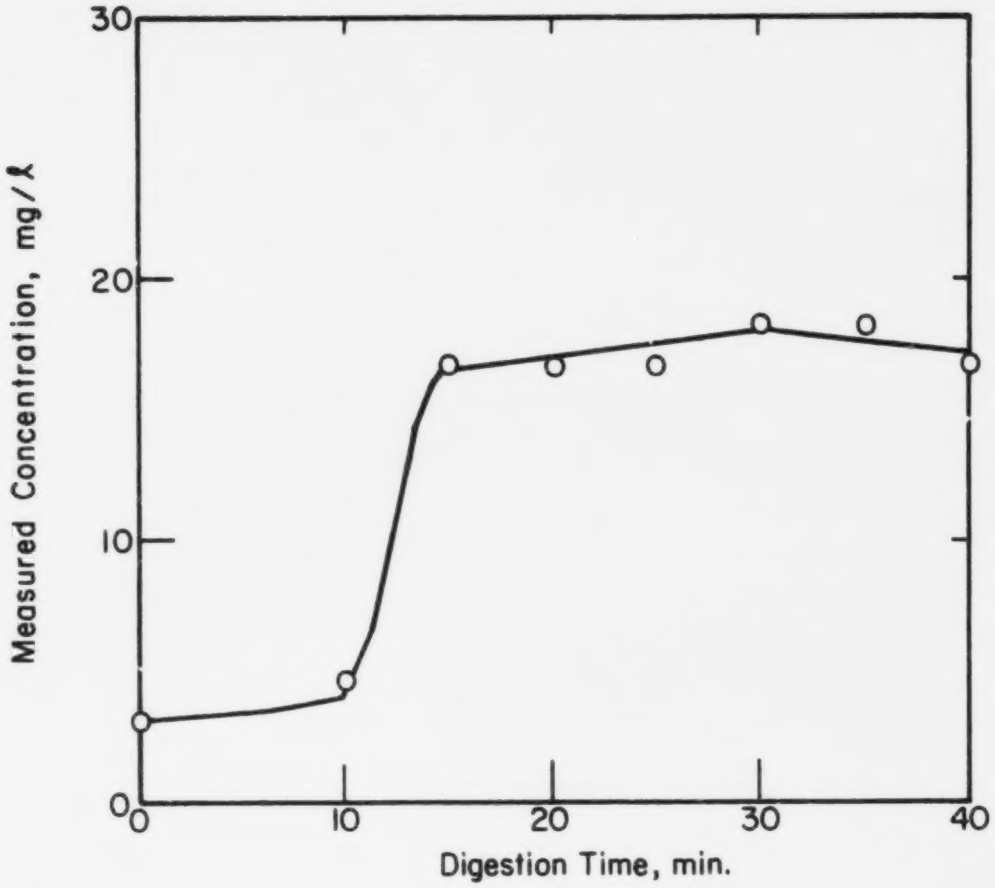

Figure 13. Effect of Digestion Time on the Concentration of Organic-N Finally Measured in the 1:10 Dilution

Standard sulfuric acid titrant, 0.02 N: prepare and standardize as directed in Alkalinity, section 8.4. For greatest accuracy, standardize the titrant against an amount of sodium carbonate which has been incorporated in the indicating boric acid solution to reproduce the actual conditions of the sample titration. A standard acid solution, exactly 0.0200 N, is equivalent to 280 μg N per 1.00 mℓ." (Standard Methods, 13th Ed., 1971, p. 245).

Procedure

"Selection of sample volume: Place a measured sample into an 800-mℓ Kjeldahl flask. Determine the sample size from the following tabulation:

| Organic Nitrogen in Sample, mg/ℓ | Sample Size, mℓ |
|---|---|
| 0-1 | 500 |
| 1-10 | 250 |
| 10-20 | 100 |
| 20-50 | 50.0 |
| 50-100 | 25.0 |

If necessary, dilute the sample to 300 mℓ and neutralize to pH 7.

Ammonia removal: Add 25 mℓ phosphate buffer solution to a sample. Add a few glass beads or boiling chips and boil off 300 mℓ. If desired, distill this fraction and determine the ammonia nitrogen. Alternatively, if ammonia has been determined by the distillation method, use the residue in the distilling flask for the organic nitrogen determination.

Digestion: Cool and add carefully 50 mℓ digestion reagent (or substitute 10 mℓ conc. $H_2SO_4$, 6.7 g $K_2SO_4$, and 1.5 mℓ mercuric sulfate solution). Then digest for an additional 30 min. Allow flask and contents to cool; dilute to 300 mℓ with ammonia-free water and add 0.4 mℓ phenolphthalein indicator solution and mix. Tilt the flask and add, carefully approximately 50 mℓ hydroxide-thiosulfate reagent to form an alkaline layer at the bottom of the flask.

Connect the flask to the steamed-out distillation apparatus and shake the flask to insure complete mixing. Add more hydroxide-thiosulfate reagent in the prescribed manner if a red phenolphthalein color fails to appear at this stage.

Distillation: Distill and collect 200 mℓ distillate below the surface of 50 mℓ boric acid solution. Use plain boric acid solution when the ammonia is to be determined by nesslerization and use indicating boric acid for a titrimetric finish. Extend the tip of the condenser well below the level of boric acid solution and do not allow the temperature in the condenser to rise above 29° C. Lower the collected distillate free of contact with the delivery tube and continue distillation during the last minute or two to cleanse the condenser.

Final ammonia measurement: Determine the ammonia by titrating the ammonia in the distillate with standard 0.02 N sulfuric acid titrant until the indicator turns a pale lavender.

Blank: Carry a blank through all the steps of the procedure and apply the necessary correction to the results.

$$\text{mg}/\ell \text{ organic N} = \frac{(\text{D-E}) \times 280}{\text{m}\ell \text{ sample}}$$

where D = m$\ell$ $H_2SO_4$ titration for sample and E = m$\ell$ $H_2SO_4$ titration for blank." (Standard Methods, 13th Ed., 1971, p. 246).

# SECTION 8

# INORGANIC CHEMICAL PARAMETERS

The inorganic pollutants may constitute approximately half of the total pollutants in recently generated leachate but represent the major part in biologically stabilized leachate. Several of the inorganic pollutants are conservative and are not rapidly removed during soil attenuation.

## 8.1 THE CHLORIDE DETERMINATION

Chloride is one of the major anions in leachate and is sometimes used as a tracer for leachate monitoring in soils because of its inert character. All methods are based on the formation of a complex or precipitate by a metal chloride. The EPA (1974) recommends the mercuric nitrate method based on the formation of the soluble mercuric chloride complex for wastewater samples and the ferricyanate method for automated analyses. Technicon (1973) also uses this method, in which the mercury, added as mercuric thiocyanate, forms a complex with chlorides. The liberated thiocyanate then reacts with ferric ions to form a colored cyanide complex.

### Interferences

Of the three chloride methods listed in Standard Methods, the argentometric method and the mercuric nitrate method are most susceptable to interferences. The argentometric method uses $AgNO_3$ to precipitate the $Cl^-$ and the red $Ag_2CrO_4$ complex to indicate the endpoint of the titration. This test is interfered with by more than 10 mg/l iron since it will mask the color of the endpoint (APHA, 1971).

The more tedious mercuric nitrate method uses $Hg\ NO_3$ to form $HgCl_2$ while the endpoint is indicated by the purple mercuric diphenyl carbazone complex. This test is interfered with by more than 10 mg/l ferric, chromate, and sulfite ions. According to Ulmer (1974) the test is also interfered by zinc and ferrous ion in excess of 100 mg/l, copper ion in excess of 50 mg/l and ferric ion in excess of 20 mg/l in the final dilution of the leachate sample.

### Previous Studies

An evaluation of two leachate samples tested with the mercuric nitrate method at a dilution of 1:10 and with one standard addition of 25 mg/l $Cl^-$ in the final dilution, showed that 96.8 percent and 100 percent was recovered, respectively (Ulmer, 1974). This would indicate that at these dilutions no interferences are encountered for these specific leachate samples. Strongly polluted and colored leachate samples, however, may not experience such a good recovery due to the interferences listed above. For that reason the potentiometric method is recommended by Standard Methods for samples that have a strong color. In addition, the method is less tedious than the mercuric nitrate method and many samples can be determined in a short period of time.

Most studies analyzing leachate selected the mercuric nitrate method while some studies used the argentometric method which is based on the formation of a AgCl precipitate after addition of $AgNO_3$. Three studies used the potentiometric determination when strong color would interfere with other methods. Two studies used the automated ferricyanide method.

Evaluation of the Method

Since many constituents present in leachate such as iron, zinc and sulfide interfere with the mercuric nitrate and argentometric method, the potentiometric method was evaluated for leachate. The method is based on the titration of the sample with $AgNO_3$, while the decrease of the chloride concentration or the increase of the $Ag^+$ concentration after the chloride is precipitated as AgCl, is measured with a Cl electrode or Ag/AgCl electrode, respectively.

Chlorides in polluted water samples can be determined with the solid state chloride electrode since common ions such as sulfate, nitrate and phosphate do not interfere. The solid-state electrode also permits measurements in the presence of oxidizing agents such as $Fe^{3+}$ and $Cu^{2+}$. Interference is caused by ions that complex the chloride and $NH_4^+$ at a concentration of 12 percent of that of chloride will result in a 1 percent error (Orion, 1970). In the leachate sample analyzed, the $NH_4^+$ value was 86 percent of the Cl value indicating that some interference may occur.

The procedures for chloride analysis using the potentiometric method establish first a calibration curve between the chloride concentration and the electrode potential. The data in Figure 14 show a linear decrease in potential at increasing concentrations. At very high concentrations the decrease may be more than linear on a normal-log plot since the activity of the chloride ion becomes substantially less than the corresponding concentration.

The chloride concentration in the leachate sample can be determined by both the direct reading and the titration method both employing standard additions. In the first method, increasing amounts of chloride are added to the sample, after which a direct potentiometric reading is made and the resulting value is converted into actual concentration with the aid of the calibration curve. The results in Figure 15 indicate that both the 1:2 and 1:4 dilution experienced a 24 percent and 26 percent enhancement, respectively. Extrapolation of the values obtained eliminated this effect, and a chloride concentration of 700 mg/l in the undiluted leachate sample was calculated.

The second method employed titration with $AgNO_3$ of leachate samples containing increasing amounts of $Cl^-$. The endpoint of the titration is indicated by the inflection point of the potentiometric reading. Figure 16 shows a titration curve of a 1000 mg/l chloride solution and the 1:2 and 1:4 diluted leachate samples indicating that a very distinct inflection point

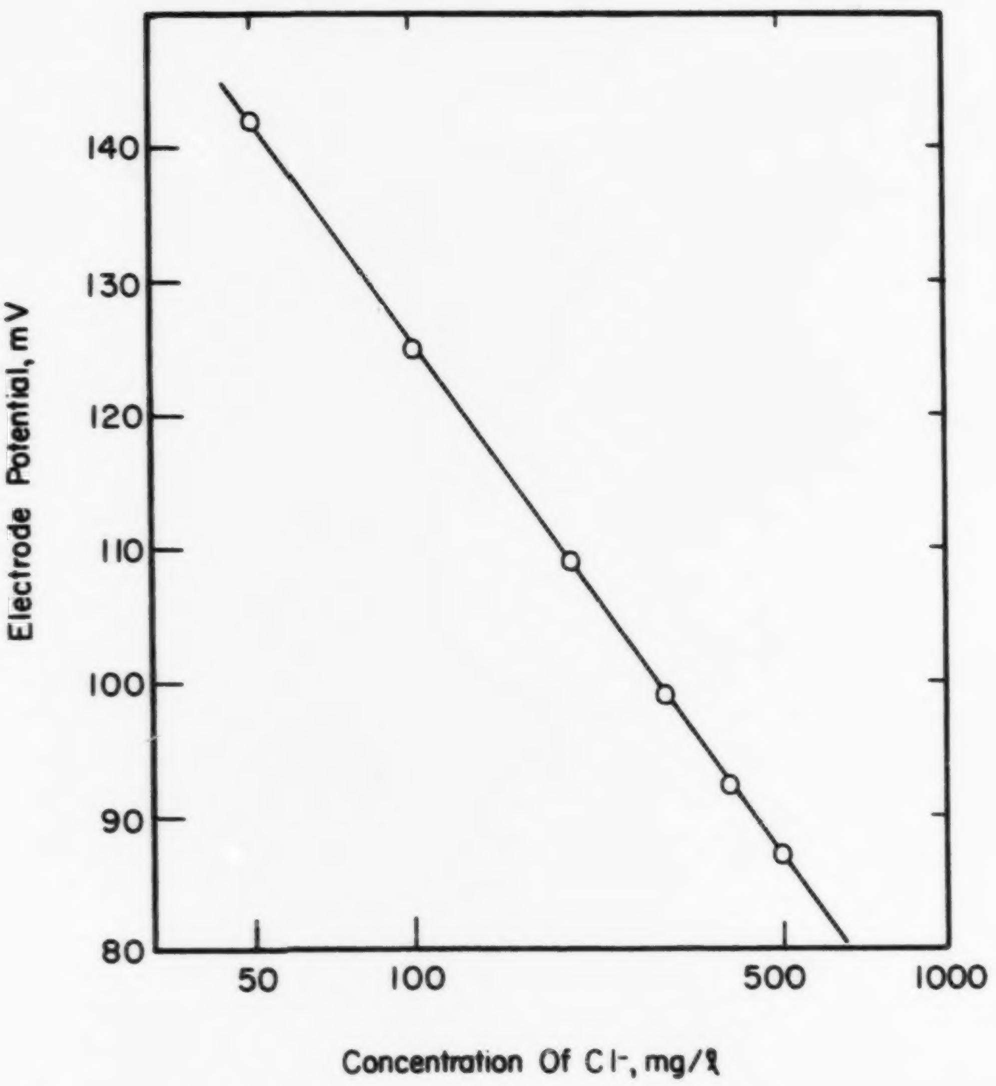

Figure 14. Calibration Curve of the Chloride Electrode

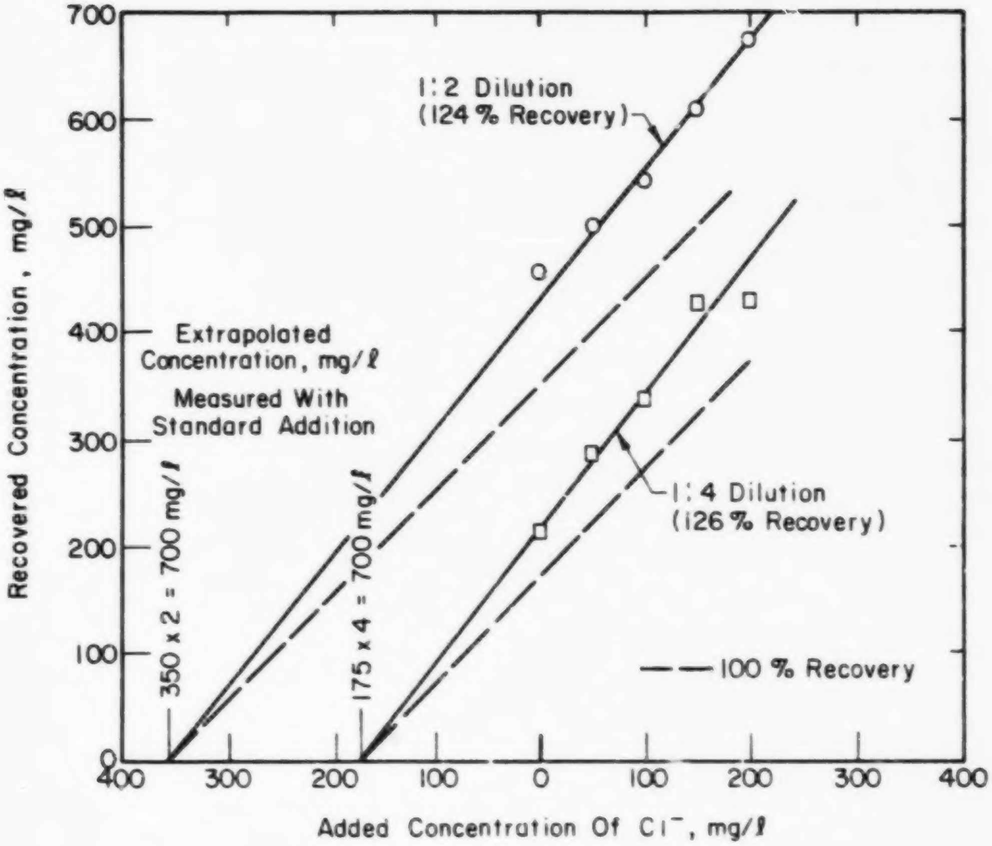

Figure 15. Chloride Determination Using Direct Potentiometric Readings in the Diluted Leachate Sample

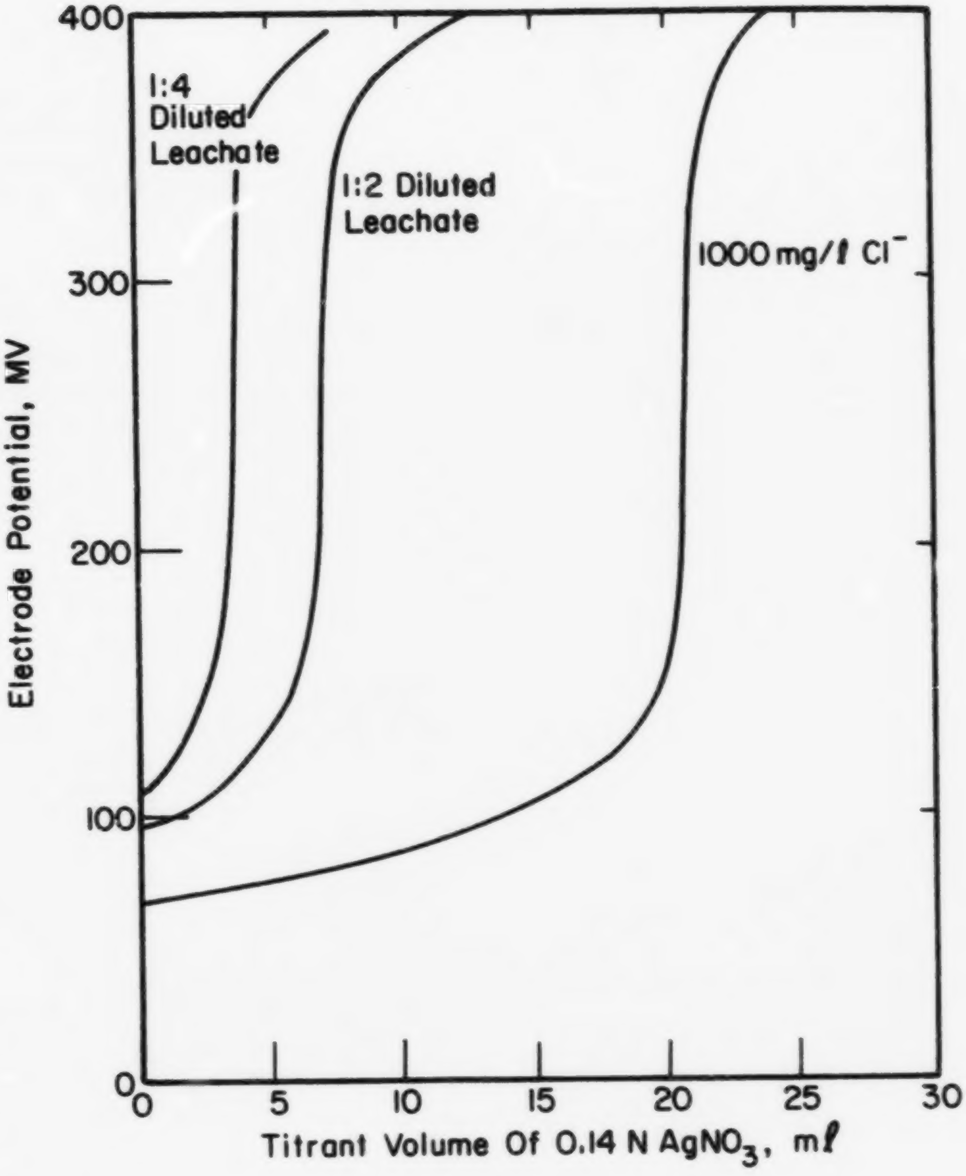

Figure 16. Titration Curve of 1000 mg/ℓ $Cl^-$ Solution and a 1:2 and 1:4 Diluted Leachate Sample

can be obtained. In order to determine the normality of the $AgNO_3$ solution, solutions of increasing $Cl^-$ content are titrated till the inflection point. Figure 17 shows that this results in a calculated normality of 0.138 N as compared to a normality calculated from the weighting of the dry $AgNO_3$ of 0.14 N.

Analysis of the leachate samples showed that approximately 100 percent of the amount of chloride added is recovered. The measurements at the 1:2 and 1:4 dilution resulted in a $Cl^-$ value in the original leachate sample of 680 mg/ℓ (Figure 18). As 100 percent of the added amount of $Cl^-$ is recovered and no enhancement is observed, the obtained value of 680 mg/ℓ is more accurate than the 700 mg/ℓ calculated from the direct readings using the standard addition method. Since no enhancement or depression occurs as a result of the presence of pollutants in leachate, the leachate sample can be titrated directly and no standard additions have to be made. Since a single titration to the inflection point is less time consuming than the direct potentiometric readings on leachate samples containing increasing standard additions, the titration method is recommended for leachate analysis. Also, it was observed that 5-10 minutes were required to stabilize the potentiometric reading when the concentration was determined directly, while the rapid increase near the inflection point was observed without any delay. On the other hand the amplitude of oscillation was smaller at high concentrations and larger near the inflection point. However, this did not cause any inaccuracy in the determination.

### Recommendations

It is recommended that in biologically stabilized leachate samples in which the color does not cause any interference, the chloride determination be conducted with the mercuric nitrate method while in strongly polluted leachate the chlorides be determined with the potentiometric titration method.

### Reagents

"Standard sodium chloride solution, 0.0141 N - Dissolve 8.243 g NaCl, dried at 105° C, in distilled water and dilute to exactly 500 mℓ. Dilute 50.0 mℓ of this solution to exactly 1,000 mℓ. The final solution contains 0.500 mg Cl per 1.00 mℓ.

Nitric acid, conc.

Standard silver nitrate titrant, 0.014 N - Dissolve 2.40 g $AgNO_3$ in distilled water and dilute to 1,000 mℓ.

Sulfuric acid, 1 + 1

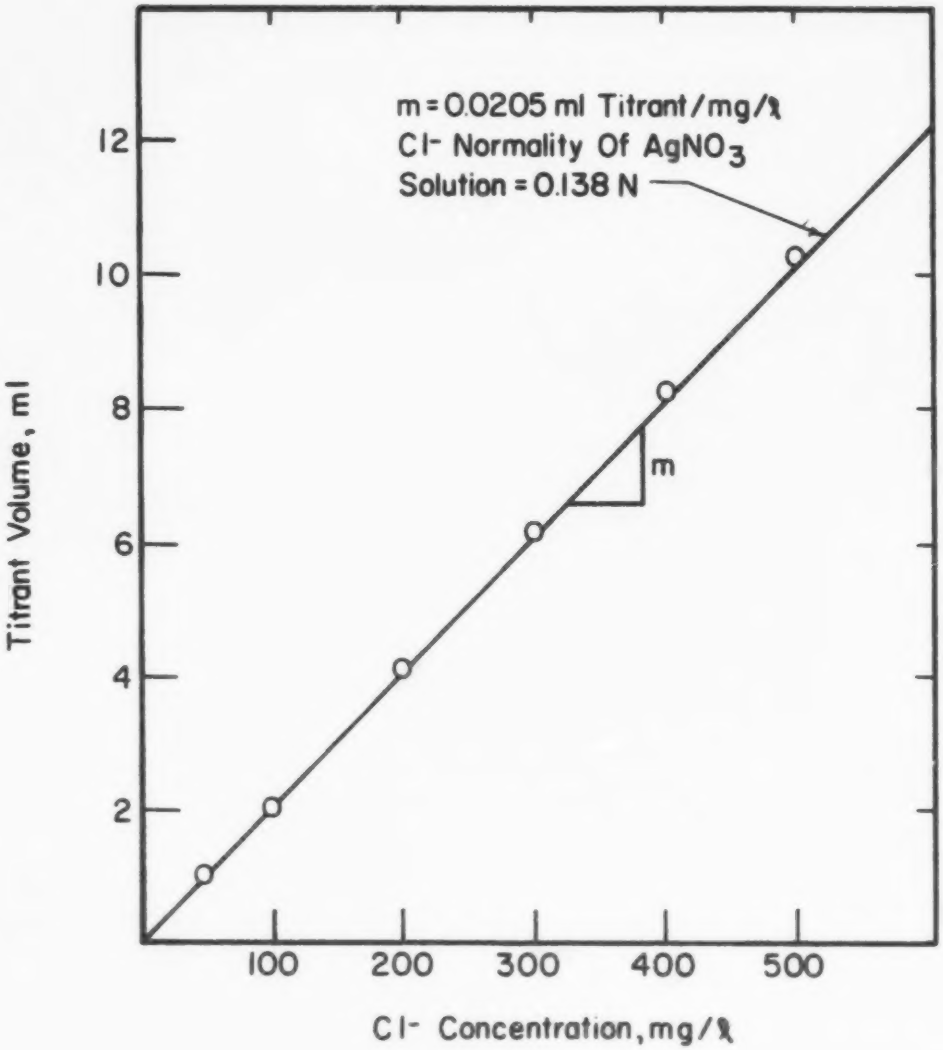

Figure 17. Determination of Normality of $AgNO_3$ Solution

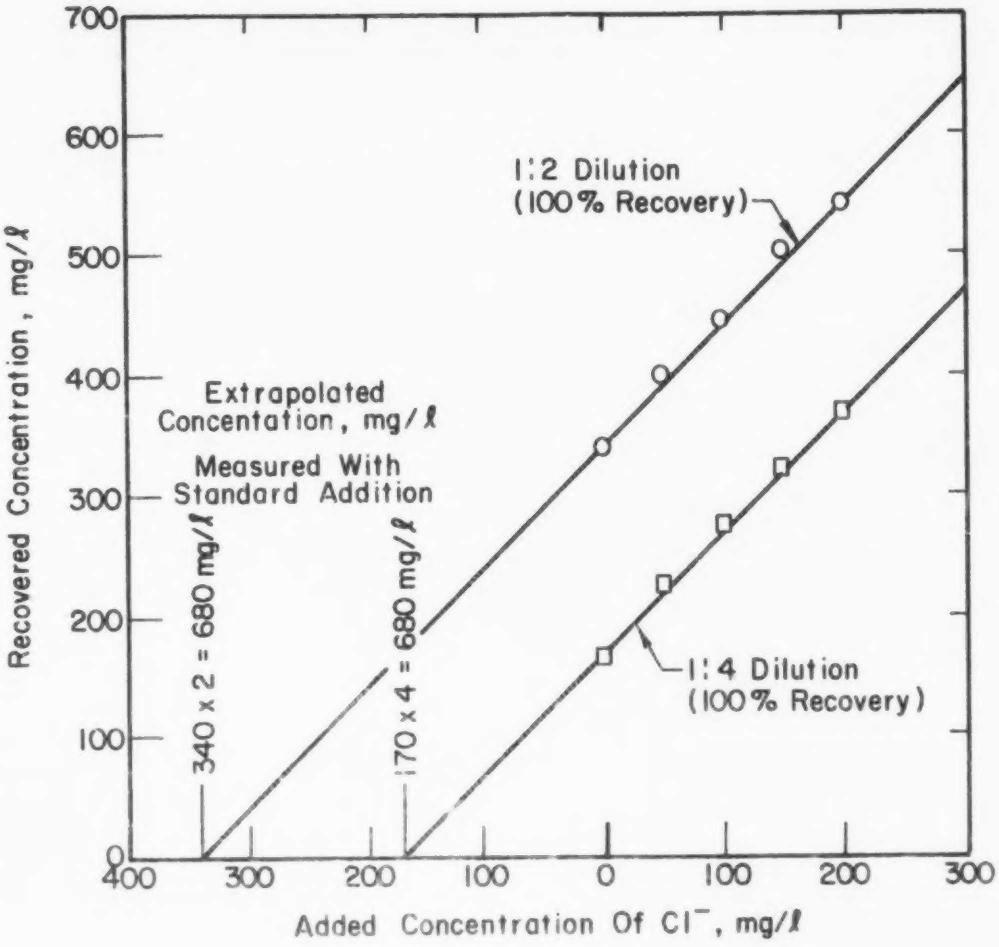

Figure 18. The Chloride Determination by the Standard Addition Method Using Titration to Inflection Point in the Diluted Leachate Sample

Hydrogen peroxide, 30 percent

Sodium hydroxide, 1 N" (Standard Methods, 13th Ed., 1971, p. 378).

### Procedure

"Inasmuch as the various instruments that can be used in this determination differ in operating details, the manufacturer's instructions should be followed. Necessary mechanical adjustments should be made. Then, after allowing sufficient time for warm-up (10 min), the internal electrical components are balanced to give an instrument setting of 0 mV or, if a pH meter is used, a pH reading of 7.0.

Place 10.0 mℓ standard NaCl solution in a 250 mℓ beaker, dilute to about 100 mℓ, and add 2.0 m conc. $HNO_3$. Immerse the stirrer and the electrodes in the solution.

Set the instrument to the desired range of millivolts or pH units. Start the stirrer.

Add standard $AgNO_3$ titrant, recording the scale reading after each addition. At the start, large increments of $AgNO_3$ may be added; then, as the end point of the reaction is approached, smaller and equal increments (0.1 or 0.2 mℓ) should be added at longer intervals, so that the exact end point can be determined. Determine the volume of $AgNO_3$ used at the point at which there is the greatest change in instrument reading per unit addition of $AgNO_3$. Adjust the $AgNO_3$ titrant to the same normality as the NaCl solution; 1.00 mℓ = 0.500 mg Cl.

$$\text{Normality of } AgNO_3 = \frac{10.0 \times 0.0141}{\text{mg } AgNO_3}$$

Pipet exactly 100.0 mℓ of sample, or an aliquot containing not more than 10 mg chloride, into a 250 mℓ beaker.

In the presence of organic compounds, sulfite or ferric iron and sulfide acidify the sample with $H_2SO_4$, using litmus paper. Boil for 5 min to remove volatile compounds. Add more $H_2SO_4$, if necessary, to keep the solution acidic. Add 3 mℓ $H_2O_2$ and boil for 15 min, adding chloride-free distilled water to keep the volume above 50 mℓ. Dilute to 100 mℓ, add NaOH solution dropwise until alkaline to litmus, then 10 drops in excess. Boil for 5 min, filter into a 250 mℓ beaker, and wash the precipitate and paper several times with hot distilled water. This step can be omitted when it is shown that it does not result in higher measured chloride concentrations.

Add conc. $HNO_3$ dropwise until acidic to litmus paper, then 2.0 mℓ in excess. Cool and dilute to 100 m if necessary. Immerse the stirrer and the electrodes in the sample and start the stirrer. After making the necessary adjustments of the instrument according to the manufacturer's instructions, set the selector switch to the appropriate setting for measuring the difference of potential between the electrodes.

Complete the determination by titrating. For the most accurate work, a blank titration should be made by carrying chloride-free distilled water through the procedure.

$$\text{mg}/\ell\ \text{Cl}^- = \frac{(A-B) \times N \times 35.45 \times 1{,}000}{D}$$

where A = mℓ $AgNO_3$, B = mℓ blank, N = normality of titrant, and D = mℓ sample." (Standard Methods, 13th Ed., 1971, p. 378-379).

## 8.2 THE SULFATE DETERMINATION

### Principle

Sulfate is present in relatively high concentrations in leachate generated from a recently leaching fill, but will decrease in concentration under anaerobic conditions in which it is reduced to sulfide, which will then precipitate heavy metals. The sulfate can be determined gravimetrically as the $BaSO_4$ precipitate or turbidimetrically. In the gravimetric method $BaCl_2$ is added to the sample and after digestion the $BaSO_4$ precipitate is filtered and weighed after drying at 105° C or ignition after 1 hour at 800° C. In the turbidimetric method the turbidity of the $BaSO_4$ precipitate is measured against a standard. The automated EPA method (1974) uses barium chloranilate that when added to the sample releases the $Ba^{++}$ which then precipitates as $BaSO_4$ while the released acid chloranilate forms a red color. Technicon (1973) uses $BaCl_2$ which is added to the sample while the excess Ba reacts with methylthymol blue to give a blue colored complex.

### Interferences

Suspended matter and silicates are precipitated and filtered together with the $BaSO_4$ precipitate. This will lead to relatively high readings, while incorporation of alkali metals in the sulfate precipitate frequently yield low results. Heavy metals may also restrict the complete precipitation of the barium sulfate. The turbidimetric method is interfered by color and suspended matter. High concentrations of $Ca^{++}$, $Mg^{++}$ and $Fe^{++}$ interfere by precipitating the chloranilate in the EPA method (1974) or react with methylthymol blue in the Technicon method and are therefore first removed by passing through an ion exchange column. However, due to organic matter chelation and formation of ferrihydroxide colloids this removal is not always successful.

## Previous Studies

Most studies selected the gravimetric method with or without ignition of the residue. A significant number of leachate analyses (Appendix A and B), generally conducted by consulting firms, use the turbidimetric method despite the strong interferences of the suspended matter and color of the leachate. Wilson (1972) noted that this method could not detect concentrations below 4 mg/ℓ. One study uses the atomic absorption technique while one study uses the methylthymol blue method.

## Evaluation of the Method

The gravimetric method specifies that the measurement of the $BaSO_4$ precipitate is conducted after digestion, filtration and drying. The dried residue can be heated to 800° C to expel occluded water or to remove colloidal organics. However, since this ignition step complicates the procedure, the method was first evaluated without the heating at 800°C.

The sample was first acid digested at pH 4 at boiling temperature. The digestion was continued until all the brown colloids of ferric hydroxide in the leachate had disappeared. After addition of the warm $BaCl_2$ a precipitate was formed. The precipitate was digested at 80° C for both 2 and 18 hours.

It was found that the digestion of the $BaSO_4$ precipitate had to be proceeded for at least 18 hours to form a readily filterable precipitate. Extended digestion also reduced the amount of the precipitate in the sample blank i.e. the leachate sample with all the reagents added, except the $BaCl_2$. When the digestion was extended from 2 hrs to 18 hrs, the precipitate in the sample blank decreased from 26.5 mg/ℓ to 10.5 mg/ℓ with the 1:2 diluted sample. The 1:2 dilution gave a precipitate some 30 times higher than that of the 1:4 diluted sample blank indicating that the acid to leachate ratio has to be sufficiently high or the leachate sufficiently dilute in order to reduce the amount of suspended solids in the digested leachate sample. Low dilutions of the leachate sample should also be avoided, since the time for filtration becomes very long (20-30 minutes) as a result of the high concentration of precipitate. Also there is an increased tendency for the solids to adhere to the wall of the filter holder.

Evaluation of the standard addition method with the 1:2 and 1:4 diluted leachate samples showed that the solids in the leachate caused a slight enhancement of the sulfate concentration by 6 percent and 2 percent, respectively (Figure 19). This again confirmed the earlier conclusion

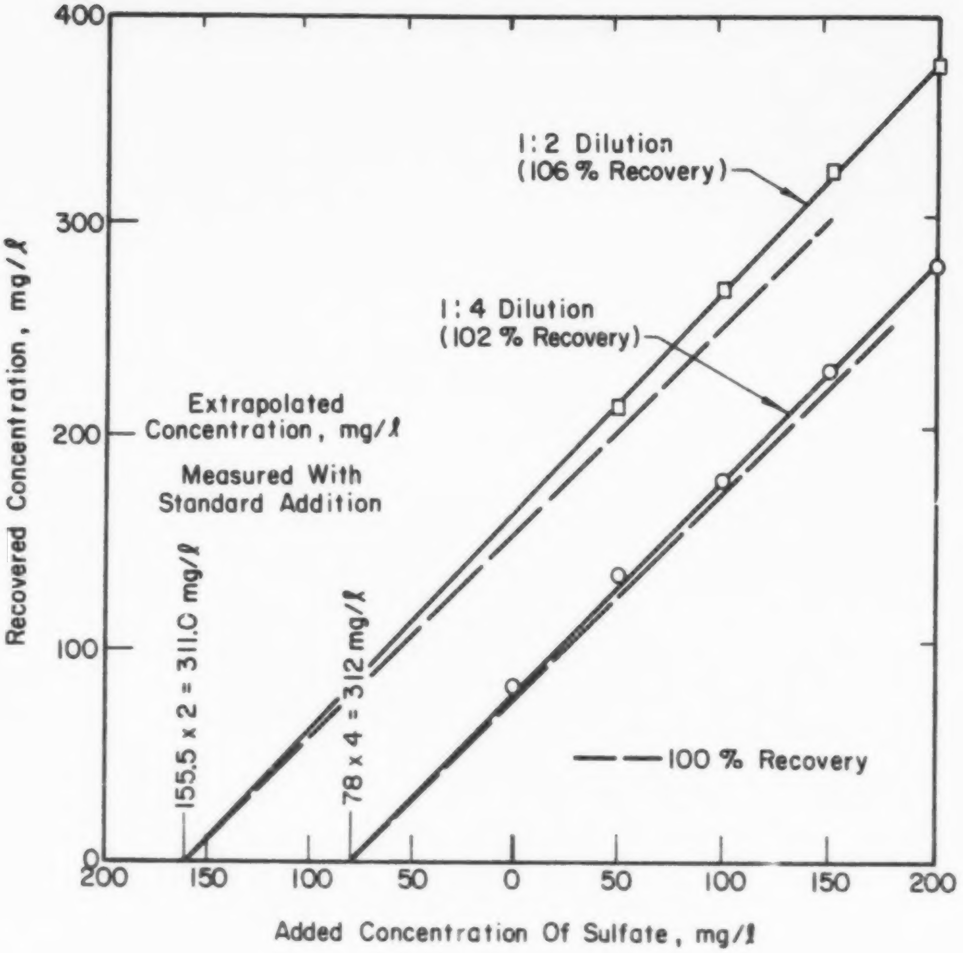

Figure 19. The Sulfate Determination with the Gravimetric Method in the 1:2 and 1:4 Diluted Leachate Samples

that low dilutions should be avoided. The 2 percent enhancement in the recovery of sulfate with 1:4 diluted sample also shows that it is not necessary to dry the residue at 800° C for the accuracies generally desired in leachate analysis.

### Recommendations

It is recommended that the gravimetric method be selected for sulfate analysis as opposed to the turbidimetric method. The automated methods are applicable only when the color and cations are sufficiently removed.

### Reagents

"Methyl red indicator solution: Dissolve 100 mg methyl red sodium salt in distilled water and dilute to 100 mℓ.

Hydrochloric acid, 1 + 1.

Barium chloride solution: Dissolve 100 g $BaCl_2 \cdot 2H_2O$ in 1 liter distilled water. Filter through a membrane filter or hard-finish filter paper before use; 1 mℓ of this reagent is capable of precipitating approximately 40 mg $SO_4$.

Silver nitrate-nitric acid reagent: Dissolve 8.5 g $AgNO_3$ and 0.5 mℓ conc. $HNO_3$ in 500 mℓ distilled water." (Standard Methods, 13th Ed., 1971, pp. 331-332).

### Procedures

"Precipitation of barium sulfate: Adjust the sample to contain approximately 50 mg of sulfate ion in a 250 mℓ volume. Adjust the acidity with HCl to pH 4.5-5.0, using a pH meter or the orange color of methyl red indicator. Then add an additional 1 to 2 mℓ HCl. Lower concentrations of sulfate ion may be tolerated if it is impracticable to concentrate the sample to the optimum level, but in such cases it is better to fix the total volume at 150 mℓ. Heat the solution to boiling and, while stirring gently, add warm barium chloride solution slowly until precipitation appears to be complete; then add about 2 mℓ in excess. If the amount of precipitate is small, add a total of 5 mℓ barium chloride solution. Digest the precipitate at 80-90° C, preferably overnight.

Preparation of filters:

1. Silica or porcelain crucible - Dry to constant weight in an oven maintained at 105° C or higher, cool in a desiccator, and weigh. Constant weight is defined as a change of not more than 0.5 mg in two successive operations consisting of heating, cooling in a desiccator, and weighing.

2. Fritted-glass filter - Dry as in 1.

3. Membrane filter - Place the filter on a piece of filter paper or a watch glass and dry to constant weight in a vacuum oven at 80° C, while maintaining a vacuum of at least 64 cm of mercury, or in a conventional oven at a temperature of 103-105° C. Cool in a desiccator and weigh the membrane only.

Filtration and weighing: Filter the barium sulfate at room temperature. Wash the precipitate with several small portions of warm distilled water until the washings are free of chloride, as indicated by testing with silver nitrate-nitric acid reagent. If the membrane filter is used, add a few drops of anticreep solution to the suspension before filtering and also to the wash water to prevent adherence of the precipitate to the holder. Dry the filter with precipitate by the same procedure used in the preparation of the filter. Cool in a desiccator and weigh.

$$\text{mg}/\ell\ SO_4 = \frac{\text{mg } BaSO_4 \times 411.5}{\text{m}\ell\ \text{sample}}$$

(Standard Methods, 13th Ed., 1971, p. 332-333).

## 8.3 THE PHOSPHATE DETERMINATION

### Principle

Phosphate is generally present in the form of orthophosphates, condensed phosphates and organically bound phosphates. In the phosphate analysis the specific phosphorus form is converted after digestion to soluble orthophosphate which is then determined colorimetrically. The specific phosphorus form can be separated into dissolved or particulate phosphorus by filtering through a 0.45 $\mu$ membrane. Orthophosphates are those phosphates that respond to the colorimetric test without preliminary hydrolysis or oxidative digestion. The condensed phosphates are those that are acid hydrolyzed at 100° C. Organic phosphates are those that are converted to orthophosphate after oxidative destruction or digestion of the organic matter.

The perchloric acid digestion method is the most drastic, dangerous and time consuming method, followed in complexity by the nitric acid-sulfuric acid method. The persulfate method is the simplest but should be evaluated for its efficiency. Most colorimetric methods are based on the formation of a blue colored complex when molybdate reacts with phosphate in stannous chloride, ascorbic acid or aminonaphthol sulfonic acid, respectively. EPA (1974) recommends the persulfate digestion followed by the ascorbic acid colorimetric method. For automated procedures they also recommend the ascorbic acid method. Technicon (1973) autoanalyzers used the ascorbic acid method but replaced the persulfate digestion with concentrated sulfuric acid digestion. For early models, Technicon recommended the aminonaphthol sulfonic acid method.

Total phosphate and to a lesser extent orthophosphate is an important parameter to be measured in leachate since aerobic biological treatment of leachate requires relatively large quantities of phosphate that sometimes have to be supplied to the treatment unit. Sufficient phosphate is generally available to sustain anaerobic biological processes. Phosphates present in leachate may reach surface waters and stimulated nuisance algal growth.

### Interferences

According to Standard Methods the vanadate and $SnCl_2$ method are interfered with by more than 100 mg/ℓ $Fe^{2+}$ and 1000 mg/ℓ $Fe^{3+}$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$ and $NH_4^+$, which are often present in those concentrations in leachate. The ascorbic acid method is generally not interfered by these substances. High iron concentrations, however, may result in an iron phosphate precipitate that may settle in the bottom of the test tube. The aminonapthol sulfonic acid method is also relatively free of interferences as compared to the other methods, and only nitrite and sulfide, generally not present in high concentrations, cause interference (ASTM, 1969).

### Previous Studies

None of the previous studies used the perchloric acid digestion and prefer the sulfuric acid-nitric acid digestion followed by the $SnCl_2$ method. Recent studies generally use the persulfate digestion. The State Water Resources Control Board of California accomplished digestion by pressure cooking in an autoclave (Appendix A). Foree and Cook (1972) dried the sample with $MgCl_2$ and heated the residue at 600° C for 10 minutes. Fungaroli (1971) used the aminonaphthol sulfonic acid method when high concentrations of organic matter were present. Otherwise he used the $SnCl_2$ method, but did not specify the concentration above which he used the former method. Pohland (1972) first used the Hach method but later selected the more accurate aminonaphthol sulfonic acid method.

The aminonaphthol sulfonic acid method was evaluated by Ulmer (1974) for a 1:10 diluted Boone County leachate sample after addition of a standard amount of 1 mg/ℓ of both organic and inorganic phosphate. It was found that leachate generally gave a slightly enhanced recovery of organic phosphates, since the recovery of barium fructose 6-phosphate increased from 86.3 percent to 86.7 percent, of 3-adenylic acid increased from 91.3 percent to 92.6 percent when compared with the recovery in distilled water. On the other hand, the recovery of glycerophosphate decreased from 99.6 percent to 98.6 percent. The simultaneous evaluation of the vanadomolybdophosphoric acid and stannous chloride methods showed that no reliable results could be obtained.

The recovery of inorganic phosphate was slightly reduced in leachate since 102 percent was recovered in water and 100 percent in leachate. No evaluation was made, however, of the digestion procedure to convert the organic phosphates to ortho-phosphate. Only one dilution was evaluated and one standard addition was tested. In addition, the method has not been used in many studies since it is not listed in Standard Methods.

A comparison of the stannous chloride method, the vanadate yellow method and the ascorbic acid method using sodium glycerophosphate as a standard, showed that ascorbic acid method gave results 6 percent higher than the stannous chloride method and 1 percent higher than the vanadate yellow method (Kaylor, 1971). Using one standard addition, Kaylor (1971) noted a 94 percent recovery of the vanadate yellow method using quench water.

### Evaluation of the Method

As the ascorbic acid method is listed in Standard Methods and is relatively free of interferences, this method was selected for evaluation. The ortho-P results showed that very high recoveries were observed when increasing amounts of $KH_2PO_4$ were added to the 1:4 and 1:6 diluted leachate samples (Figure 20). In both cases 100 percent of the amount added was recovered, a result similar as obtained by Ulmer (1974) with aminonaphthol sulfonic acid. Although the recoveries were very high, a slight reduction at higher dilutions was noted since the 1:4 dilution resulted in an extrapolated value of 0.09 mg/ℓ or 0.36 mg/ℓ in the undiluted leachate, while the 1:6 dilution gave an extrapolated value of 0.055 mg/ℓ or 0.33 mg/ℓ in the undiluted sample, which is 8 percent lower than the 1:4 dilutions. Related studies in this laboratory showed that increasing dilutions caused a more rapid oxidation of the iron to the ferric form which then may precipitate ortho phosphates, causing a relative reduction in its concentration at higher dilutions. The sample should therefore be kept anaerobic and as little dilution as possible should be used.

A very important aspect of the total-P determination is the digestion step in which the organic phosphates are coverted to the ortho form. Recent studies have shown that the less tedious persulfate digestion is preferred above the more rigorous sulfuric acid-nitric acid digestion as long as the method gives good recovery. Increasing amounts of persulfate were therefore added to the sample diluted to 140 mℓ. The results in Figure 21 show that increasing values are obtained by increasing the amount of digestion reagent. A noticeable shoulder, however, is observed at a concentration of 400 mg/100 mℓ sample, and further increase of the measured concentration is probably due to enhancement of the reading by the digestion reagent itself. The amount of 750 mg/100 mℓ sample as recommended by Standard Methods should therefore be reduced to 400 mg/100

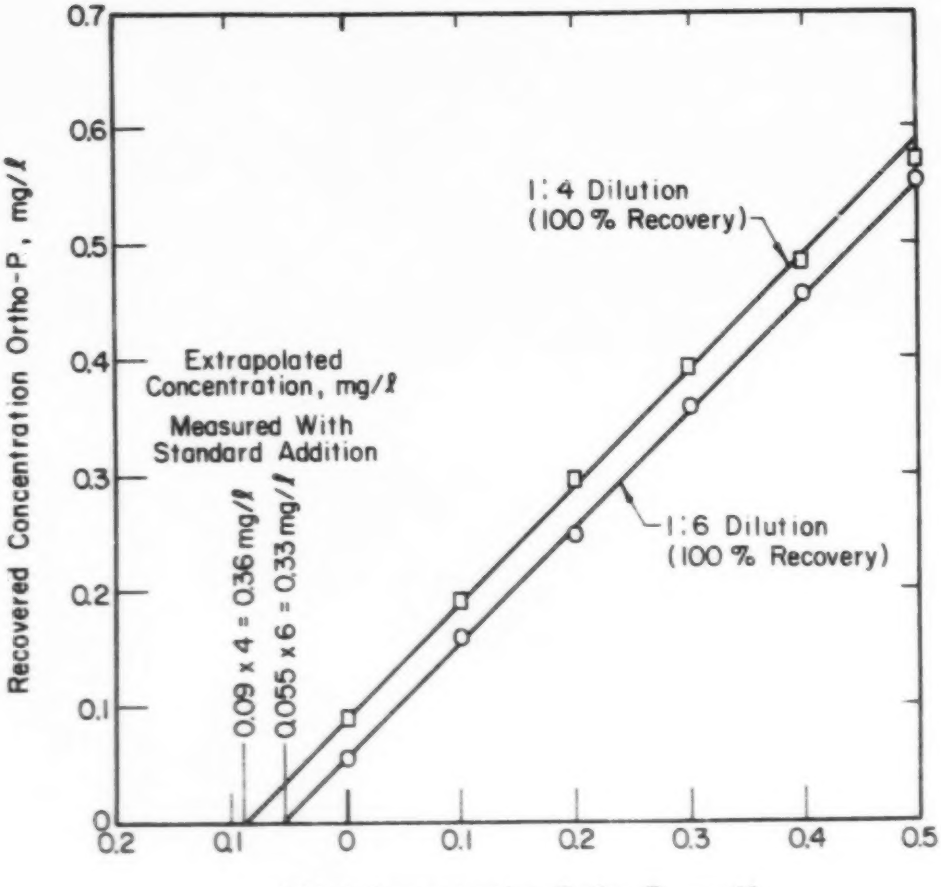

Figure 20. The Ortho Phosphate Determination with the Ascorbic Acid Method in 1:4 and 1:6 Diluted Leachate Samples

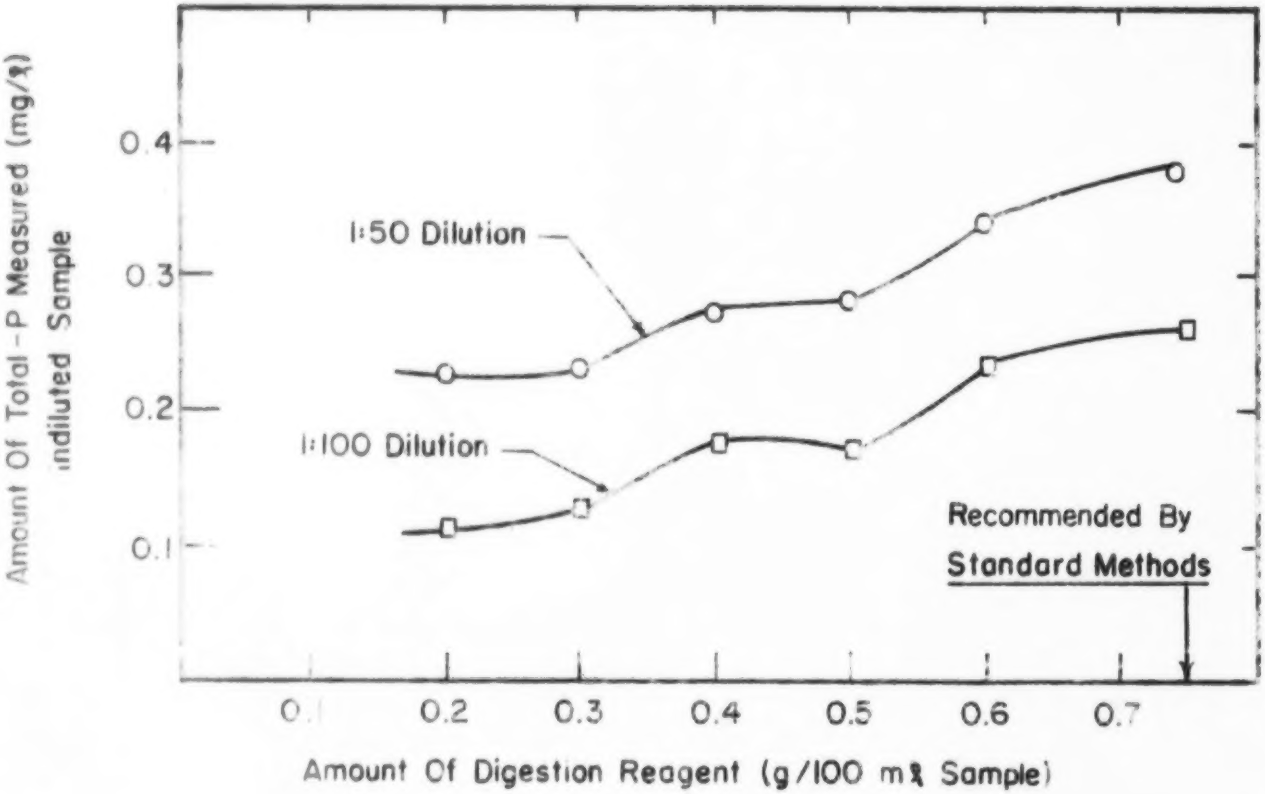

Figure 21. Effect of Amount of Digestion Reagent on the Results of the Total P Determination

mℓ when analyzing leachate. A substantial dilution effect was also observed since the 1:50 dilution resulted in a concentration of 13.5 mg/ℓ in the undiluted leachate sample while the 1:100 dilution gave 17.5 mg/ℓ.

Evaluation of the digestion time (Figure 22) showed that a 30 minute digestion time in the autoclave at 15 psi and 250° C is sufficient to hydrolyze all the organic phosphate. A similar dilution effect was observed in that the 1:100 dilution resulted in a calculated value of 16.5 mg/ℓ in the original leachate sample while the 1:250 dilution gave a result of 32 mg/ℓ.

In order to determine the effect of different dilutions the standard addition method was used in the 1:50 and 1:100 dilution using DNA which consists of organic P for 9.3 percent of its weight, and added in increasing amounts to the sample. Figure 23 shows that a substantial depression of 27.5 percent was observed for the 1:50 dilution which was reduced to 17 percent in the 1:100 dilution. Extrapolation of the observed values resulted in a calculated value of 19.5 mg/ℓ for the 1:100 dilution and 16 mg/ℓ for the 1:50 dilution indicating that the standard addition method in the 1:50 dilution negates only part of the interference.

The last phase of the evaluation therefore consisted of the determination of the optimum dilution for measuring the total phosphate. Tests were run on leachate samples of increasing dilutions. The results in Figure 24 show that the calculated total P values in the leachate reach a plateau value of 19 mg/ℓ up to a dilution of 1:200, indicating that at this dilution the interferences in the leachate have been diluted out. A further rise at 0.095 mg/ℓ is attributed to the inability of the test to give a proportionally decreasing color intensity at decreasing concentrations. The Standard Methods listed 0.01 mg/ℓ as the lower limit of this test which is 10 times lower than that found in the present study.

## Recommendations

It is recommended that the aminonaphthol sulfonic acid or the ascorbic acid method be used to measure total-P concentration in leachate employing the persulfate digestion. The amount of recommended persulfate digestion reagent is 400 mg/100 mℓ sample while the digestion time recommended by Standard Methods is sufficient to hydrolyze the P. The ortho-P test as determined by the ascorbic acid method does not experience significant interference and should be run on the anaerobically stored leachate samples after as little dilution as possible. In order to obtain reliable results, a standard addition curve as shown in Figure 22 be established or a progressive dilution curve be made as shown in Figure 23, for the total P determination. Such steps are not necessary for the ortho-P determination.

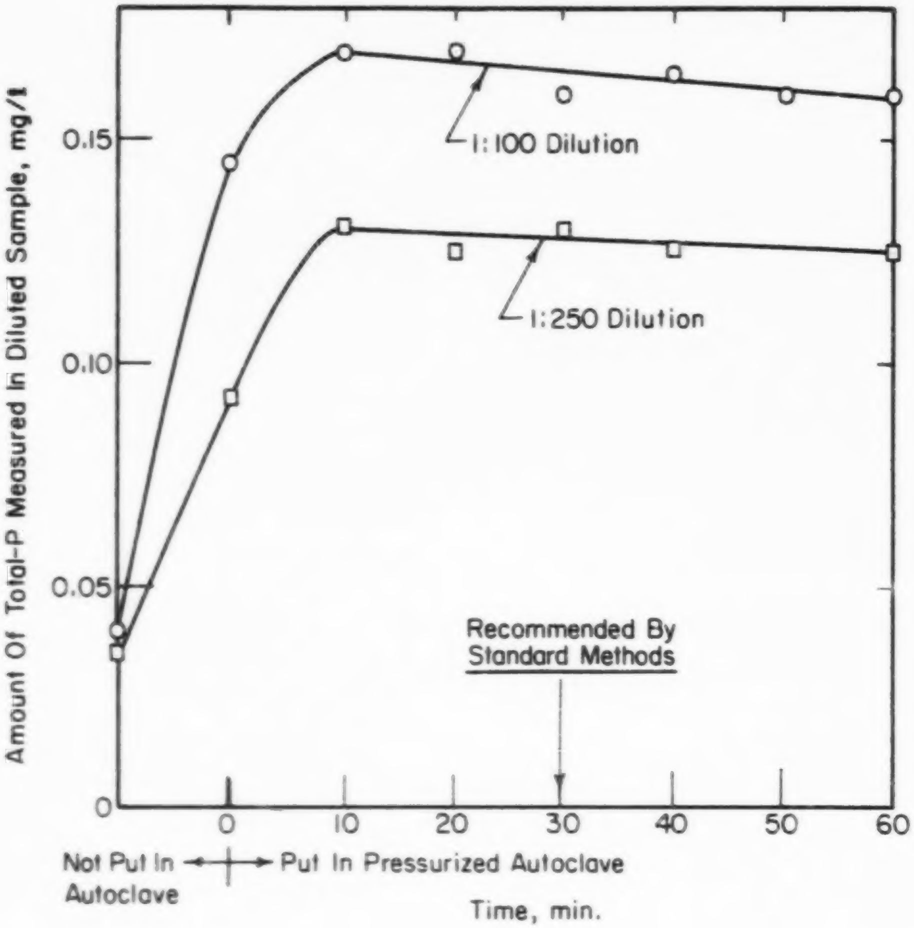

Figure 22. Effect of Digestion Time on the Result of the Total P Determination

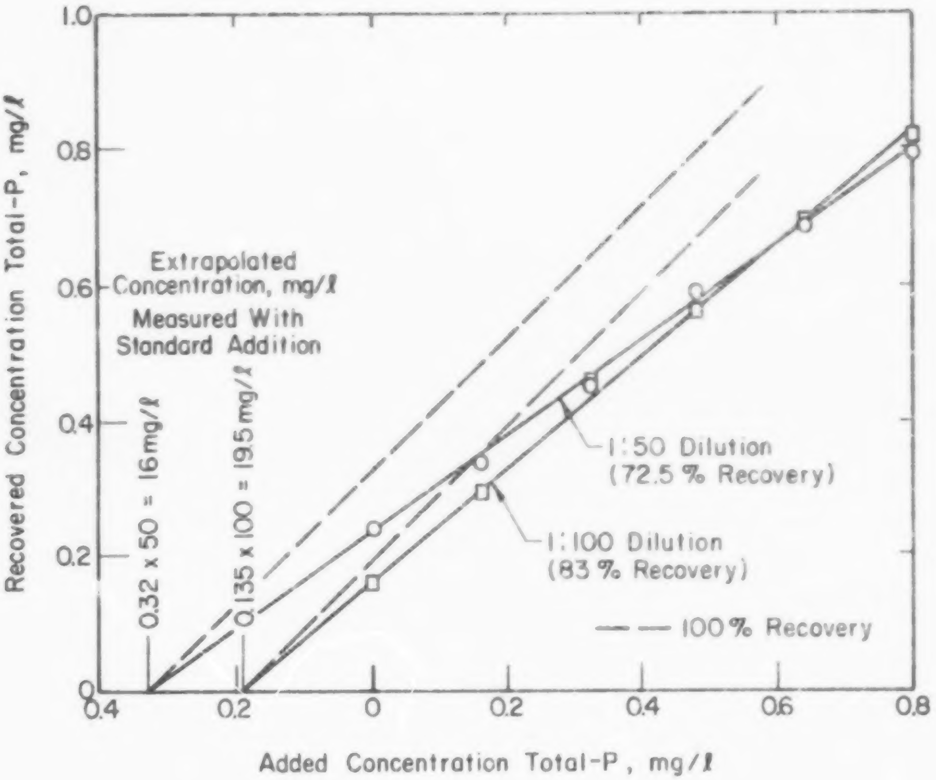

Figure 23. The Total-P Determination with the Ascorbic Acid Method in the 1:50 and 1:100 Diluted Leachate Sample Using the Standard Addition Method

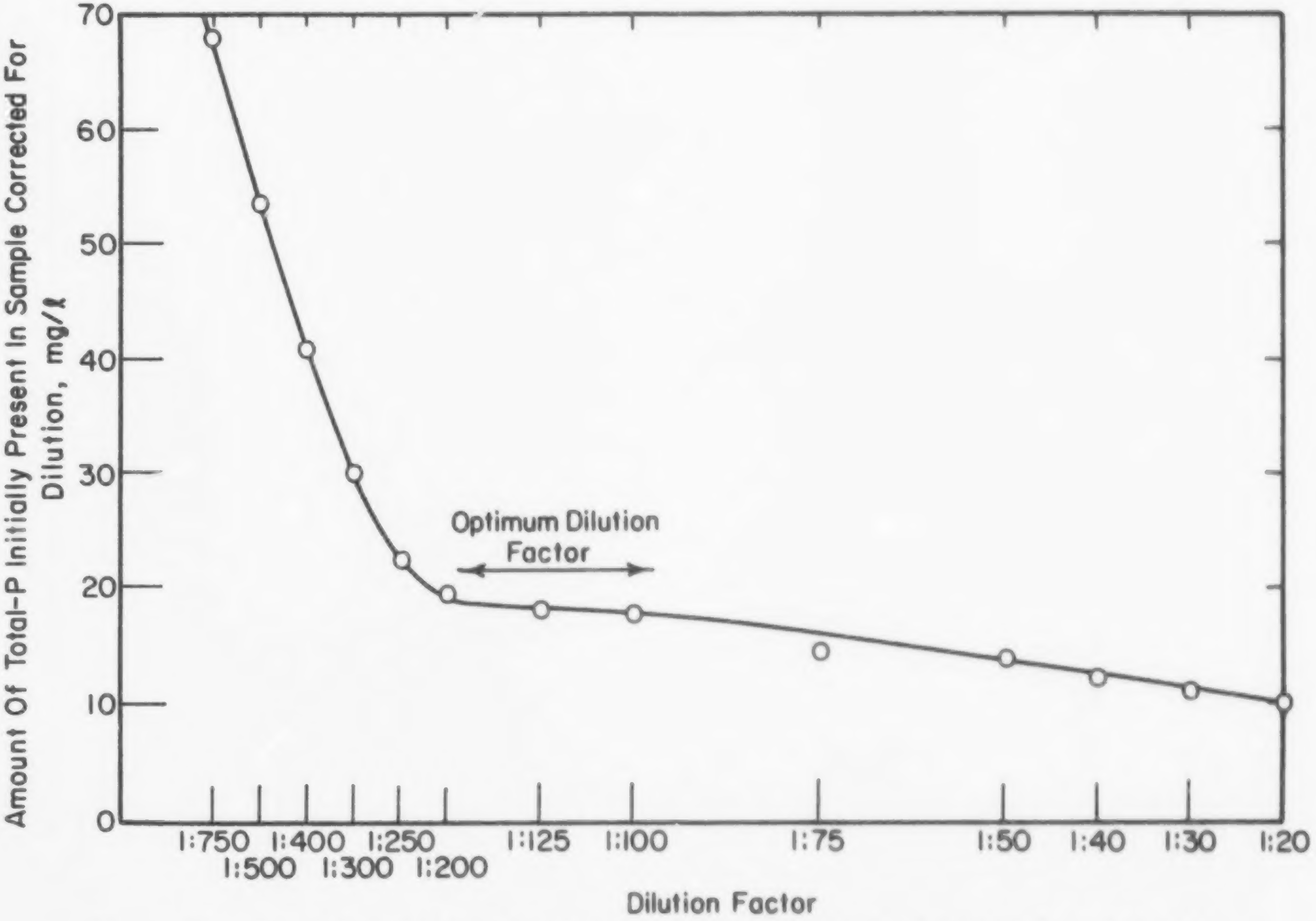

Figure 24. The Total-P Determination with the Ascorbic Acid Method in a Leachate Sample Using the Progressive Dilution Method

## Reagents for the Persulfate Digestion

"Phenolphthalein indicator solution.

Sulfuric acid solution: Carefully add 300 mℓ conc. $H_2SO_4$ to approximately 600 mℓ distilled water and then dilute to 1 liter with distilled water.

Potassium persulfate solution: Dissolve 2.7 g $K_2S_2O_8$ in 100 mℓ distilled water. Prepare daily.

Sodium hydroxide, 1 N." (*Standard Methods*, 13th Ed., 1971, p. 526).

## Procedures for the Persulfate Digestion Employed in the Total P Determination

"Take 100 mℓ or a suitable aliquot of thoroughly mixed sample. To each 100 mℓ sample or aliquot diluted to 100 mℓ, add 1 drop (0.05 mℓ) phenolphthalein indicator solution. If a red color develops, add sulfuric acid solution dropwise to just discharge the color. Then add 1 mℓ sulfuric acid solution and 15 mℓ potassium persulfate solution.

Boil gently for at least 90 min, adding distilled water to keep the volume between 25 and 50 mℓ. Alternatively, heat for 30 min in an autoclave or pressure cooker at 15-20 psi. Cool, add 1 drop (0.05 mℓ) phenolphthalein indicator solution, and neutralize to a faint pink color with sodium hydroxide solution. Restore the volume to 100 mℓ with distilled water." Determine the total phosphorus present in the sample with the aminonaphthol sulfonic acid method (Ulmer, 1974) or the ascorbic acid method listed below. When the digestion step is omitted, these tests measure the ortho-P content of the sample. (*Standard Methods*, 13th Ed., 1971, p. 526).

## Reagents for the Ascorbic Acid Method Employed in the Ortho-P Determination

"*Alcohol, ethyl* (95 percent) or isopropyl.

*Sulfuric acid solution*, 5 N: Dilute 70 mℓ conc. $H_2SO_4$ with distilled water to 500 mℓ.

*Antimony potassium tartrate*: Dissolve 4.3888 g $K(SbO)C_4H_4O_6 \cdot 1/2\ H_2O$ in 200 mℓ distilled water. Store in a dark bottle at 4° C.

*Ammonium molybdate solution*: Dissolve 20 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 mℓ distilled water. Store in a plastic bottle at 4° C.

*Ascorbic acid*, 0.1 M: Dissolve 1.76 g ascorbic acid in 100 mℓ distilled water. The solution is stable for about a week if stored at 4° C.

*Combined reagent*: Mix the above reagents in the following proportions for 100 mℓ combined reagent: 50 mℓ 5 N sulfuric acid, 5 mℓ antimony potassium tartrate, 15 mℓ ammonium molybdate solution, and 30 mℓ ascorbic acid solution. Allow all reagents to reach room temperature before they are mixed, and mix in the order given. If turbidity forms in the combined reagent after the addition of antimony potassium tartrate or ammonium molybdate, shake the combined reagent and let it stand for a few minutes until the turbidity disappears before proceeding. The reagent is stable for at least 1 week if stored at 4° C.

*Stock phosphate solution*:

*Standard phosphate solution*: Dilute 50.0 mℓ stock phosphate solution to 1,000 mℓ with distilled water to form a solution containing 2.00 μg P per 1.00 mℓ." (*Standard Methods*, 13th Ed., 1971, p. 532-533).

## Procedure for the Ascorbic Acid Method Employed in the Total P Determination

"Treatment of sample: Pipet 20.0 mℓ clear sample into a clean, dry test tube or a 125-mℓ erlenmeyer flask. Add mℓ ethyl or isopropyl alcohol. Mix thoroughly. Because curves prepared with ethyl alcohol are slightly different from those prepared with isopropyl alcohol, use the same alcohol in treating samples and standards. Add 1 mℓ combined reagent. Mix thoroughly and allow to stand 10 min for color development before reading in a spectrophotometer at a wavelength of 880 nm or a filter photometer equipped with a red color filter.

Correction for turbidity or interferring color: Natural color of water generally does not interfere at the high wavelength used. In the case of highly colored or turbid samples, prepare a blank by adding all the reagents except ascorbic acid and antimony potassium tartrate to the sample. Subtract the absorbance of the blank from the absorbance of each of the unknown samples.

Preparation of calibration curve: Prepare individual calibration graphs from a series of six standards within the phosphate ranges. Use a distilled water blank with the combined reagent to make the photometric readings for the calibration curve. Plot absorbance vs phosphate concentration, which should form a straight line passing through the origin. Test at least one phosphate standard with each set of samples.

$$\text{mg}/\ell\ \text{P} = \frac{\text{mg P} \times 1{,}000}{\text{m}\ell\ \text{sample}}\ "$$

(*Standard Methods*, 13th Ed., 1971, p. 533).

## 8.4 ALKALINITY AND ACIDITY

### Principle

The alkalinity of a water is the capacity to accept protons and is determined by titrating the sample with strong mineral acid to a specified endpoint. It thus determines quantitatively the ability of a given sample to neutralize strong acids. In leachate from a recently generating fill, where the pH is acidic most of the alkalinity is due to the buffering capacity of partially dissociated free volatile fatty acids, and carboxyl groups of complex organics. In biologically stabilized leachate where the pH is generally neutral or slightly alkaline, the alkalinity is contributed by the carbonate and bicarbonate species as a result of the dissolution of the $CO_2$ gas generated during the methane fermentation.

The acidity of a water is the capacity to donate protons and is determined by titrating the sample using strong mineral base, to a specified endpoint. In leachate from a recently generating fill where the pH is acidic, most of the acidity is due to undissociated free volatile fatty acids, dissociated ammonia and other proton donors. In biologically stabilized leachate the acidity is mainly due to bicarbonate species and to a lesser extent due to dissociated ammonia. Therefore, direct relations are anticipated between alkalinity and acidity and the contributing cations and anions mentioned above. Since several constituents contribute to the alkalinity and acidity, these tests only give a very general idea of the magnitude of the pollutants and are therefore somewhat comparable to the total and volatile solids test and the conductivity measurement, although they yield less information concerning the leachate characteristics. The measurement is important when the pH of the leachate has to be adjusted to provide optimum chemical and biological treatment.

In unpolluted waters the Standard Methods recommend titration endpoints at pH 8.3 and between 5.1 and 4.5 depending on the magnitude of the alkalinity. In polluted waters it recommends an arbitrary endpoint of 8.3 (phenolphthalein endpoint) and 3.7 (methyl orange endpoint) unless a potentiometric titration curve indicates a distinct inflection point which can be employed and the endpoint should then be specified with the analysis. From the titration curve the inflection point can be determined, whereafter the amount of acid or base, expressed as $CaCO_3$ equivalent, can be calculated. The potentiometric titration is also to be used for colored or turbid waters where difficulties arise in determining a color indicator endpoint.

The EPA (1974) recommends pH endpoints of 8.2 and 4.5 which differs from the 8.3 and 3.7 as recommended by Standard Methods. The automated procedure of EPA (1974) uses methyl orange dissolved in a pH 3.1 buffer as a colorimetric test and is therefore subject to color interferences from the leachate. A similar method is used by Technicon (1973).

### Interferences

Standard Methods indicates that the acidity and alkalinity determination is not only restricted to bicarbonate species but is also contributed by other weak acids or bases and hydroxides. The test therefore only indicates general properties of the leachate and cannot be used for the quantitative determination of specific species.

### Previous Studies

Most investigators selected 4.5 or sometimes 4.3 and 4.2 as the endpoint for the alkalinity determination although Standard Mehtods does not recommend so. Although Standard Methods does not recommend so for colored samples some leachate analyses, generally conducted by commercial laboratories, used colorimetric tests. Several studies determined the titration curve and used the observed inflection point (Appendix A). However, they did not specify in their results the value of the selected pH, as is recommended in Standard Methods. One study stated that no inflection point existed. Qasim (1965) presented actual titration curves and showed inflection points at a pH of 3.8 and 7.2.

A comparison of the alkalinity determination using the potentiometric method and the methyl orange endpoint titration showed that considerably lower results were obtained with the latter method due to strong color and turbidity interferences (Hughes *et al.*, 1971).

### Evaluation of Method

Titration curves were run on leachate samples of different strength obtained from landfills of different ages to determine their inflection points. Results in Figure 25 show that the higher the COD of the polluted samples, the larger the amount of strong acid is required to reduce the pH to the inflection point of 3.2. This inflection point corresponds to the pH of the highest derivative of the titration curve for the most polluted samples. Since the weak free volatile fatty acids with pK values around 4.8 corresponding to the pH of the lowest derivative of the titration curve are major constituents in leachate, it explains the low inflection points with the polluted leachate samples.

The amount of equivalents necessary to increase the pH from 3.2 to 4.8 should be equal to the equivalents of half of the free volatile fatty acids present in the solution. Since the latter amount is more than that calculated from the gas chromatographic determination (GC), it is suggested that other weak acids, such as phosphoric acid, silicic acid, and fulvic acid, and weak bases, such as ferric hydroxide, and zinc hydroxide also contribute to the alkalinity in this pH region. The titration curve, can therefore, not be used to determine the fatty acid concentration, and other methods such as the GC and the column partition chromatographic method are more applicable.

Figure 25 also shows that the less polluted leachate samples, the inflection point increases to pH 4.6 since the alkalinity is now mainly determined by the carbonate and bicarbonate species. The bicarbonate alkalinity has a reported inflection point of 5.1 for alkalinities of about 30 mg/ℓ, pH 4.8 for 150 mg/ℓ and pH 4.5 for 500 mg/ℓ. The effect of a decreasing fatty acid concentration as measured by GC on the pH of the inflection point is shown in Figure 26. This indicates that the pH of the inflection point may be used indirectly to internally check the fatty acid data.

The acidity determination as shown in Figure 25 should be run to a pH of 7.6 for high strength leachate samples and 8.9 for less polluted samples corresponding to the measured inflection points. At a pH of 7.6 all of the free volatile fatty acids are dissociated while at a pH of 8.9 all $CO_2$ is converted to bicarbonate. Other weak acids and weak bases also contribute to the acidity.

If bicarbonate and carbonate alkalinity are desired, than the sample should be measured for Total Carbon with the Total Carbon Analyzer before and after removal of the inorganic carbon ($N_2$ stripping at pH of 2 or $CO_2$ removal at 100° C).

## Recommendations

It is recommended that alkalinity and acidity determinations be made potentiometrically on the undiluted samples and that the endpoints be used as determined from the titration curve. These endpoints should be specified in reporting the results of the analysis.

## Reagents for the Acidity Test

"Carbon dioxide-free distilled water: Prepare all stock and standard solutions, and dilution water for the standardization procedure, with distilled water which has a pH of not less than 6.0. If the water has a lower pH, it should be freshly boiled for 15 min and cooled to room temperature. Deionized water may be substituted for distilled water provided that it has a conductance of less than 2 micromhos/cm and a pH greater than 6.0."

Standard sodium hydroxide titrant, 0.02 N: Dilute 20.0 mℓ 1N NaOH with $CO_2$-free distilled water to 1 liter. Store in a tightly rubber-stoppered pyrex glass bottle protected from atmospheric $CO_2$ by a soda-lime tube. For best results, prepare weekly. Standardize the solution against 0.0200 N potassium biphthalate solution which has been prepared by dissolving 4.085 g anhydrous $KHC_8H_4O_4$, and diluting to the mark of a 1-liter volumetric flask with $CO_2$-free distilled water. Alternatively, the alkali may be standardized against standard 0.02 N HCl or $H_2SO_4$ made

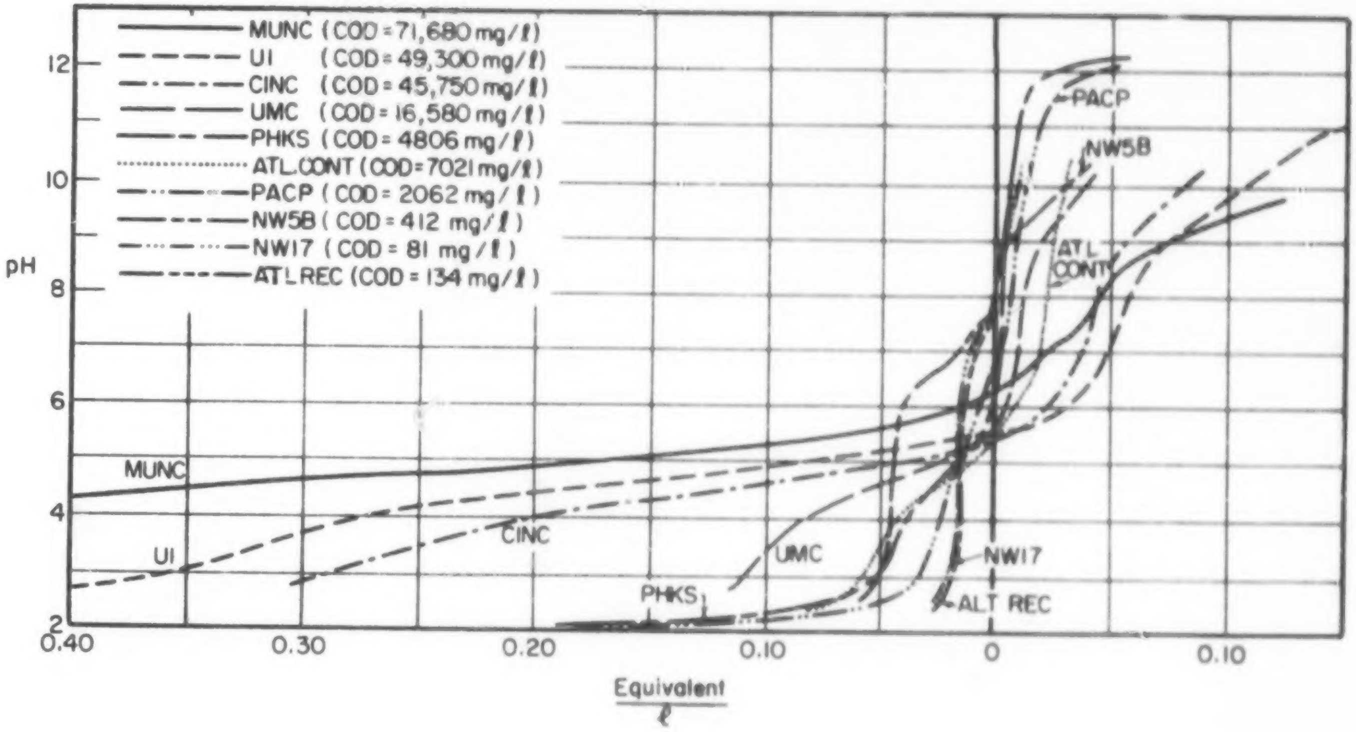

Figure 25. Titration Curves of Leachate Samples of Different Pollutional Strength

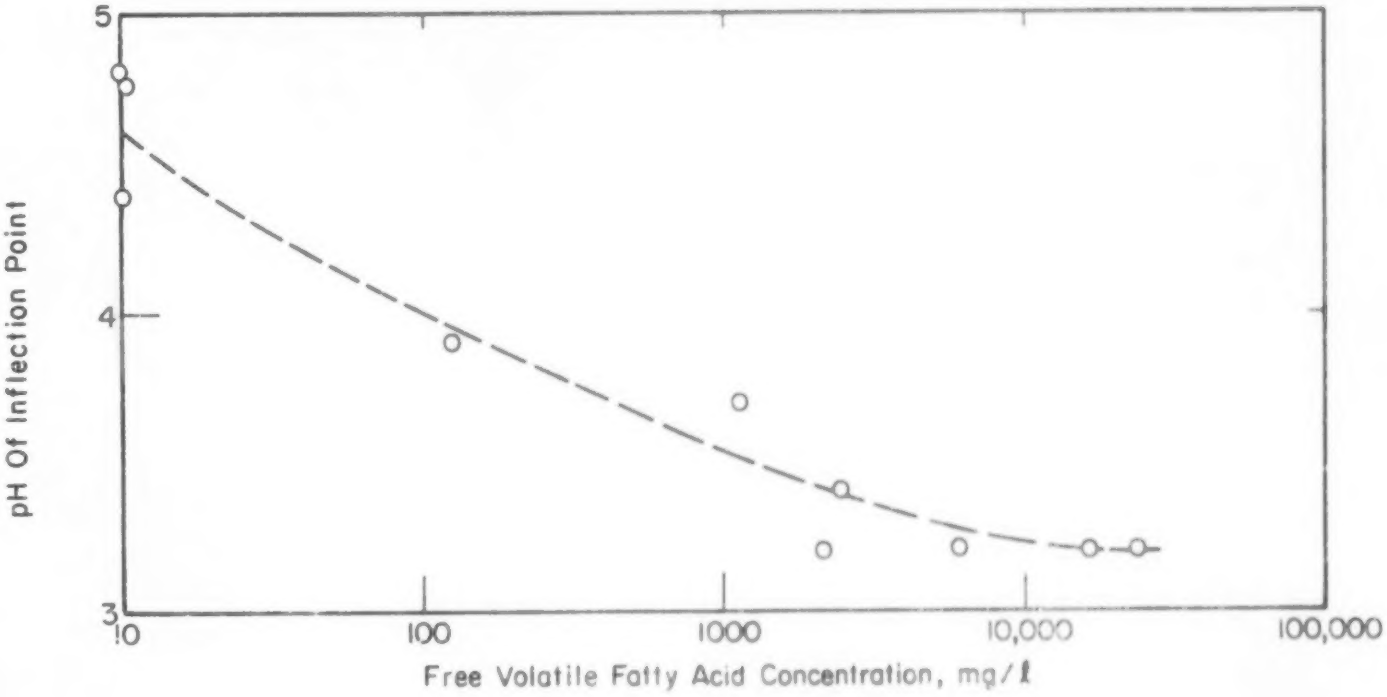

Figure 26. Effect of Free Volatile Fatty Acid Concentration on the pH of the Inflection Point of the Titration Curve

up for the alkalinity tests. Perform the standardization exactly as the typical acidity titration using the identical volumes of final solution, and the same time interval for the determination. A standard NaOH solution, exactly 0.0200 N, is equivalent to 1.00 mg $CaCO_3$ per 1.00 mℓ." (Standard Methods, 13th Ed., 1971, p. 51).

Procedures for the Acidity Test

"Titrate with standard 0.02 N NaOH until the inflection point of the titration curve as shown in Figure 25.

$$\text{Acidity as mg}/\ell\ CaCO_3 = \frac{A \times N \times 50{,}000}{m\ell\ \text{sample}}$$

where A = mℓ NaOH titrant and N = normality of NaOH." (Standard Methods, 13th Ed., 1971, p. 52).

Reagents for the Alkalinity Test

"Carbon dioxide-free distilled water: Prepare all stock and standard solutions, and dilution water for the standardization procedure, with distilled water which has a pH of not less than 6.0. If the water has a lower pH, it should be freshly boiled for 15 min and cooled to room temperature. Deionized water may be substituted for distilled water provided that it has a conductance of less than 2 micromhos/cm and a pH greater than 6.0.

Standard sulfuric acid or hydrochloric acid titrant, 0.02 N: Prepare stock solutions approximately 0.1 N by diluting either 8.3 mℓ conc. HCl or 2.8 mℓ conc. $H_2SO_4$ to 1 ℓ. Dilute 200 mℓ of the 0.1 N stock solution to 1 ℓ with $CO_2$-free distilled water. Standardize the 0.02 N acid against a 0.0200 N sodium carbonate solution which has been prepared by dissolving 1.060 g anhydrous $Na_2CO_3$ (primary standard grade), oven-dried at 140° C, and diluting to the mark of a 1 ℓ volumetric flask with $CO_2$-free distilled water. Alternatively, the acid may be standardized against standard 0.02 N NaOH prepared for the acidity test. Perform the standardization exactly as the typical alkalinity titration, using the identical volumes of final solution, sodium thiosulfate, and the same time interval as for the sample determination.

For the best results, take for standardization a volume of 0.0200 N sodium carbonate solution which approximates the average alkalinity of the water samples normally encountered in the given laboratory. A standard acid solution, exactly 0.0200 N, is equivalent to 1.00 mg $CaCO_3$ per 1.00 mℓ. (Standard Methods, 13th Ed., 1971, p. 54).

### Procedures for the Alkalinity Test

"Titrate with standard 0.02 N standard acid to the inflection point of the titration curve as shown in Figure 25, and record the volume of acid titrant.

$$\text{Alkalinity as mg}/\ell\ \text{CaCO}_3 = \frac{B \times N \times 50{,}000}{m\ell\ \text{sample}}$$

where B = mℓ standard acid titrant and N = normality of standard acid treatment. When the alkalinity of sample is so large that more than an equal volume of titrant is used to reach the equivalent point, the normality of the titrant should be increased." (Standard Methods, 13th Ed., 1971, p. 55).

## 8.5 THE NITRATE DETERMINATION

### Principle

Nitrate will generally be present in low concentrations in leachate for a recently generating fill but will increase in concentration after further stabilization of the refuse when organic nitrogen is converted to ammonia nitrogen which under oxidizing conditions is further converted into nitrate.

Nitrate is a difficult determination in the presence of interfering ions and all methods listed in Standard Methods for analysis of polluted waters are therefore tentative. The phenol disulfonic acid method produces a yellow color (measured at 410 nm) between nitrate and phenol disulfonic acid. The brucine-sulfanilic acid method, based on the reaciton between nitrate and brucine, also results in a yellow color measured at 410 nm. The chromotropic acid method is also based on the formation of a yellow colorimetric product measured at 410 nm when nitrate reacts with 4, 5-dihydroxy-2, 7-naphthalene disulfonic acid. The ultraviolet spectrophotometric method measures directly the absorbance at 220 nm while in the zinc reduction method the nitrates are reduced to nitrite which is then determined with the nitrite method.

The EPA (1974) recommends both the brucine method and the cadmium reduction method, while Technicon (1973) uses the copper-cadmium reduction method.

### Interferences

The yellow color of the phenol disulfonic acid method is interfered with by more than 10 mg/ℓ chlorides, while yellow colored materials should be absent, which makes the method less applicable to leachate (APHA, 1971).

The yellow color of the brucine sulfanilic acid method is generally not interfered by high salt concentrations, but ferrous and ferric iron will give a positive enhancement, while organic matter also gives some interference (APHA, 1971). The yellow color of the chromotrophic acid method is interfered by certain oxidants, yellow colored organic matter and certain heavy metals.

The ultraviolet spectrophotometric method is only applicable to unpolluted samples. The method is of a less accurate nature since the variable organic matter interference is only partially corrected by measuring the absorbance at the compensating wavelength of 275 nm (APHA, 1971). The zinc reduction method is interfered by reducing and oxidizing substances such as ferric ions and other heavy metals, while organics and suspended soldis interfere by coating the column. The cadmium reduction method is subject to some of the interferences listed for the zinc reduction method.

### Previous Studies

Mao and Pohland (1973) reported that the nitrate concentrations were initially determined with the specific ion electrode and colorimetrically, but that strong matrix interferences were encountered due to the presence of high iron and chloride concentration. These problems, however, were eliminated with the use of a Technicon Autoanalyzer using hydrazine as a reducing agent and measuring the formed nitrite. The Solid and Hazardous Waste Research Laboratories noted that the Cd reduction method as used in Technicon Autoanalyzers did not give satisfactory results due to coating of the column by iron and organic matter (Appendix A). The County of Sonoma and Emcon Associates (1973) found that the brucine test did not always determine nitrate concentration accurately since dissolved organic matter, iron and strong oxidizing and reducing substances were found to interfere with the test. The interferences were reduced by subtracting from the final readings the value obtained from the sample to which all the reagents were added except the brucine sulfanilic acid. Qasim (1965) used both the brucine method and the aluminum reduction method but did not indicate whether the two methods gave different results. Foree and Cook (1972) used the standard addition method for determining the nitrate concentration with the specific ion electrode after precipitation of the chloride. Most studies, however, use the brucine method (Appendix A). In order to compare the last two tests, both the nitrate electrode and the brucine method were evaluated in the present study.

### Evaluation of Methods

Comparison of the two methods showed that the nitrate electrode gave better results than the brucine sulfanilic acid method. The results of the former test, shown in Figure 27 indicate recoveries of 116 percent and 118 percent in the 1:25 and the 1:50 dilution. Figure 28 shows that the potential variation is sufficiently large to determine small differences in concentration. The readings obtained without any $NO_3$-N added to the sample were generally higher than obtained through the standard addition method. The first reading in the 1:50 diluted sample was 1.32 mg/l which is 164 percent higher then calculated with the standard addition method i.e. 0.50 mg/l. The difference in the 1:25 dilution was less pronounced than in the 1:50 dilution and the first reading without $NO_3$-N addition was 51 percent higher than calculated from the standard addition method. It is expected, however, that this difference will decrease with lower dilution and that reliable results will be obtained when the nitrate concentration is determined directly in the leachate sample without any dilution. The nitrate value obtained as a result of the test i.e. 25 mg/l is relatively high as compared to values reported in the literature, indicating that previous studies may have underestimated nitrate concentrations.

The colorimetric nitrate test gave results less reliable than obtained with the electrode. The sample would undergo a color change from light green to yellow brown when dilutions were made for the nitrate test, probably as the result of the oxidation of the iron and other metals present in the leachate. The yellow brown color absorbs at the same wavelength as the color reagent of the test thereby causing strong interference. The relative color change was more pronounced at the higher dilutions and may well explain the low recovery of 59 percent (Figure 29) observed in the 1:50 dilution. At the lower dilution of 1:25 the sample apparently oxidized less rapidly since the recovery was 82 percent. The value of 22 mg/l obtained with this test is slightly lower than the 25 mg/l obtained with the electrode, and is probably due to the interferences of the colorimetric test.

### Recommendations

It is recommended that nitrates be determined with the specific ion electrode instead of the brucine method. It is preferable to measure the nitrates with the electrode in the undiluted sample. Standard amounts should be added to the sample to determine the recovery of the method. When the brucine method is used the suspended solids and color may be removed with a massive lime dosage of 5000 to 10,000 mg/l $Ca(OH)_2$. Aluminum hydroxide is not as effective as a coagulant.

### Reagents for the Nitrate Electrode Method

"Stock potassium nitrate solution: Dissolve 721.8 mg anhydrous $KNO_3$ in distilled water and dilute to 1,000 ml. This solution contains 100 mg/l N.

Standard potassium nitrate solution: Dilute 50 ml stock potassium nitrate solution to 500 ml with distilled water; 1.00 ml = 10.0 μg N = 44.3 μg $NO_3$." (Standard Methods, 13th Ed., 1971, p. 456).

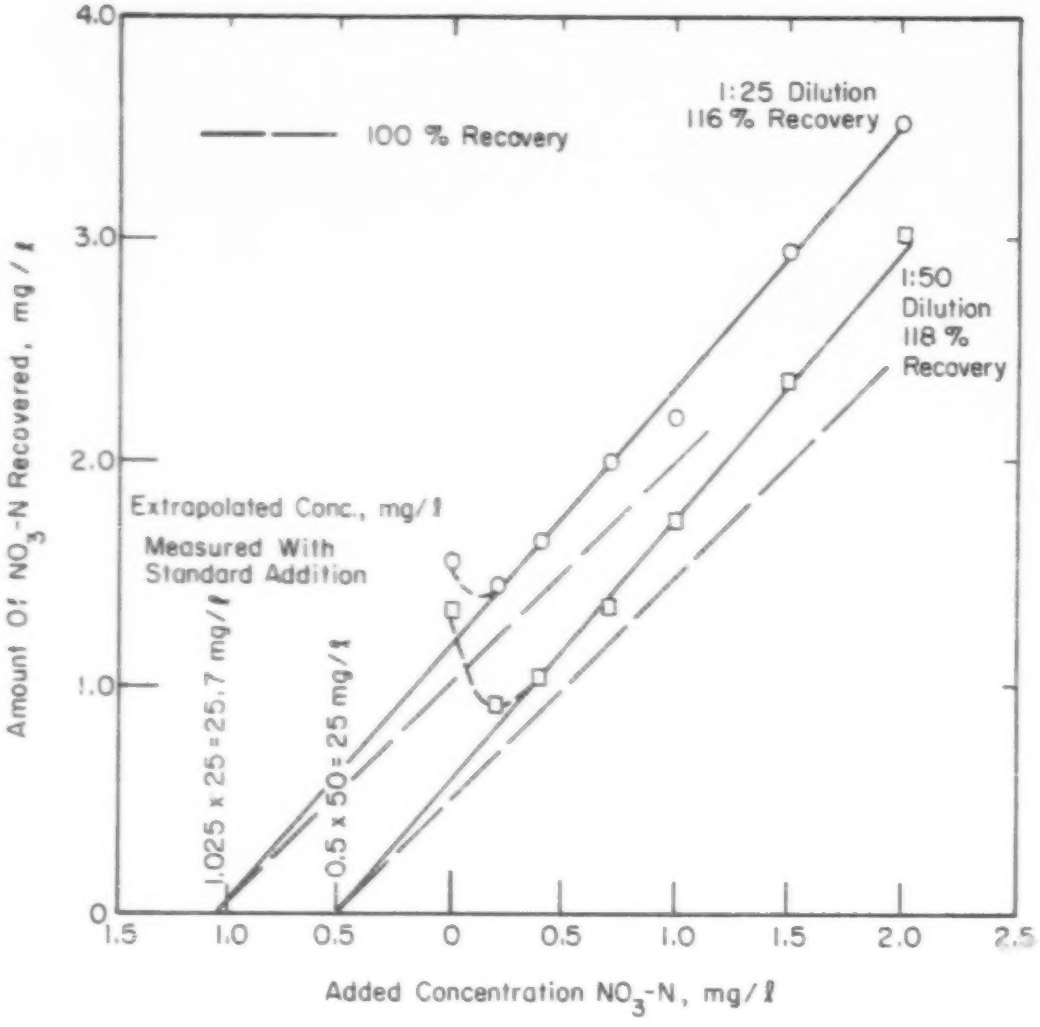

Figure 27. The Nitrate Determination with the Nitrate Electrode Using Standard Additions

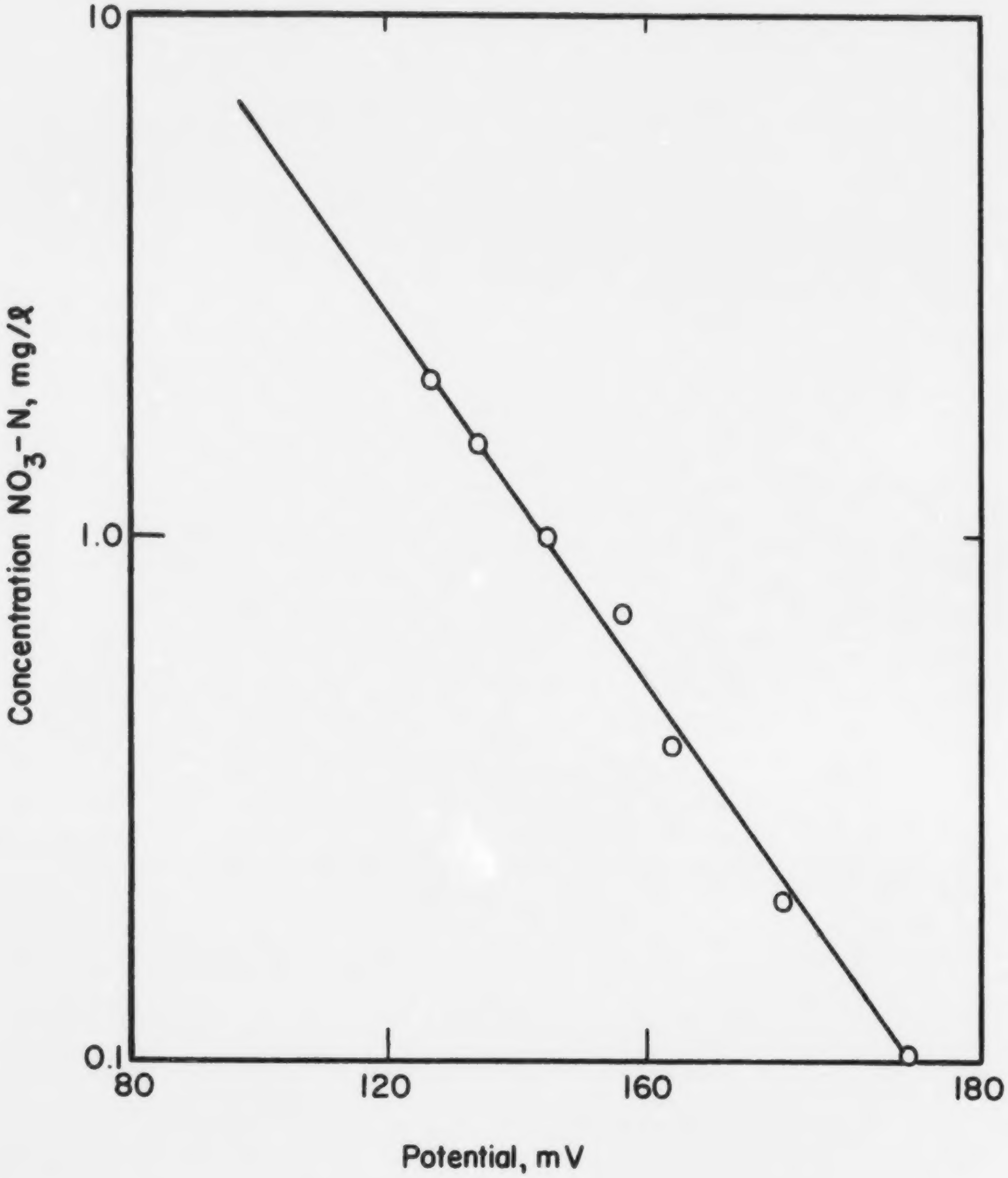

Figure 28. Calibration Curve of the Nitrate Electrode

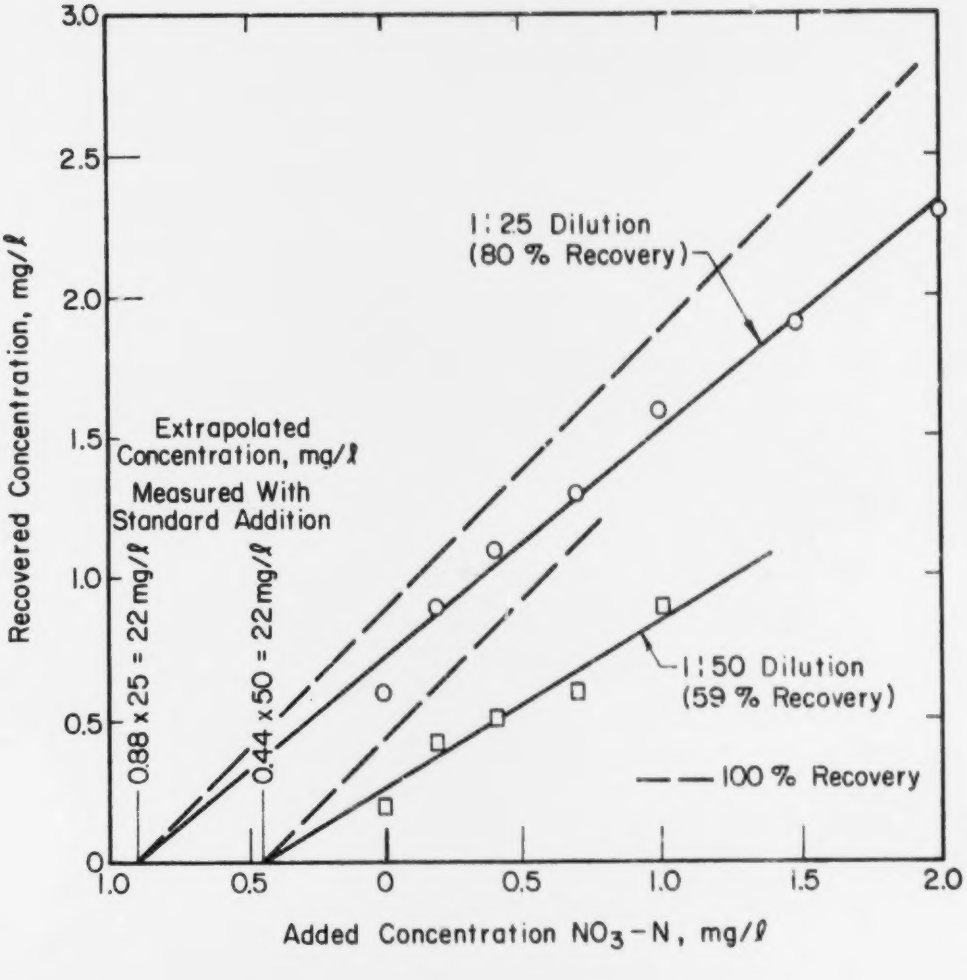

Figure 29. The Nitrate Determination with the Brucine Sulfanilic Acid Method Using Standard Additions

### Procedures for the Nitrate Electrode Method

Calibrate the electrode system against standard solutions of increasing concentrations, as shown in Figure 28, using the nitrate electrode connected with a pH meter. Because of the different makes of nitrate electrodes which are available commercially, it is not possible to provide detailed instructions for the correct operation of each electrode. In each case therefore follow the manufacturer's instructions.

Determine the potential in the sample to be measured and convert this into a nitrate concentration using the calibration curve. When making standard additions, add increasing amounts of standard solution to the sample and dilute to a specified volume. Measure the concentrations and construct a graph as shown in Figure 27. Extrapolation of the obtained values enables the calculation of the initial nitrate concentration.

## 8.6 THE NITRITE DETERMINATION

### Principle

Nitrite is an intermediate nitrogen form when ammonia is converted to nitrate. Nitrite is generally present in lower concentrations than nitrate and its determination is only useful when the nitrates are determined concurrently.

The only method that is mentioned in Standard Methods for the determination of nitrite is the naphthylamine method. A reddish purple azo dye is formed at pH 2.0 by the coupling of diazotized sulfanilic acid with naphtylamine hydrochloride. The reaction is to some extent similar to the brucine method to determine nitrate which gives a yellow color as the result of the reaction of nitrate sulfanilic acid and brucine. The EPA (1971) recommends the use of the less cancinogenic n-(1-napthyl)-ethylenediamine instead of the naphylamine.

### Interference

A precipitate of the colored complex can be caused by the presence of ferric iron and lead, while cupric ions may cause a lower reading. Interference of other ions may be reduced by EDTA addition (EPA, 1974). Colored ions will likewise interfere.

### Previous Studies

Several studies that determine nitrates do not analyze for nitrites. None of the studies that include the parameter in their measurements recommend it as an accurate method. Automated analysis (Technicon, 1973) also uses the reaction between nitrite, sulfanilamide and naphtylamine.

## Evaluation of the Method

When the test was run on an unfiltered leachate sample with standard additons of nitrite, a high nitrite concentration of 4.8 mg/ℓ was obtained while the recovery was relatively low (Figure 30). The recovery in the 1:25 dilution was 66 percent which decreased to 26.7 percent for the 1:50 dilution. Since the color of the sample was deep purple rather than pink as observed for the standards, it was suspected that a precipitate had formed. Filtration of the 1:25 diluted leachate after the color had formed caused a 60 percent decrease in absorbance while the recovery decreased from 66 percent to 39.5 percent, suggesting that the solids in the sample enhanced the absorbance. This is confirmed by the lower recovery in the 1:50 dilution (26.7 percent) as compared to the 1:25 dilution (66 percent), since increasing dilutions enhance the oxidation of the ferrous iron and the formation of suspended solids consisting of iron hydroxide. A second run was therefore made in which the leachate sample was filtered twice through a Whatman #1 filter paper prior to running the analysis. The results showed that filtration before color development caused an even further decrease in nitrite recoveries since the recovery of the 1:25 dilution decreased from 66 percent to 7.1 percent and that of the 1:50 dilution from 26.7 percent to 8.8 percent, while the extrapolated concentration decreased from 4.8 mg/ℓ to 0.8 mg/ℓ. However, at a nitrite concentration of 0.030 mg/ℓ the recovery of the 1:50 dilution showed a sharp increase approaching 100 percent. The 1:25 dilution gave this increase at a concentration of approximately 0.050 mg/ℓ. This pattern may indicate that the sample has a nitrite demand that has to be satisfied before any free nitrite will be present in the sample. This observation was confirmed in a third run in which relatively high concentrations of nitrite were added to the filtered sample and whereby the 1:25 diluted leachate sample had a recovery of 70 percent and the 1:50 diluted sample a recovery of 93 percent, while both curves showed that the sample had a nitrite demand.

The above results indicate that nitrite is likely to be absent in a polluted leachate sample obtained from a fill recently generating leachate but may be present in biologically stabilized leachate. Alleged nitrite concentrations measured are sometimes due to interferences present in the sample.

## Recommendations

It is recommended that nitrite be determined according to *Standard Methods* with additions of standard amounts of Nitrite-N to the *filtered sample*. Extreme care should be exercised in interpreting the obtained results. The napthylamine reagent should be replaced by the n-(1-napthyl) ethylene diamine.

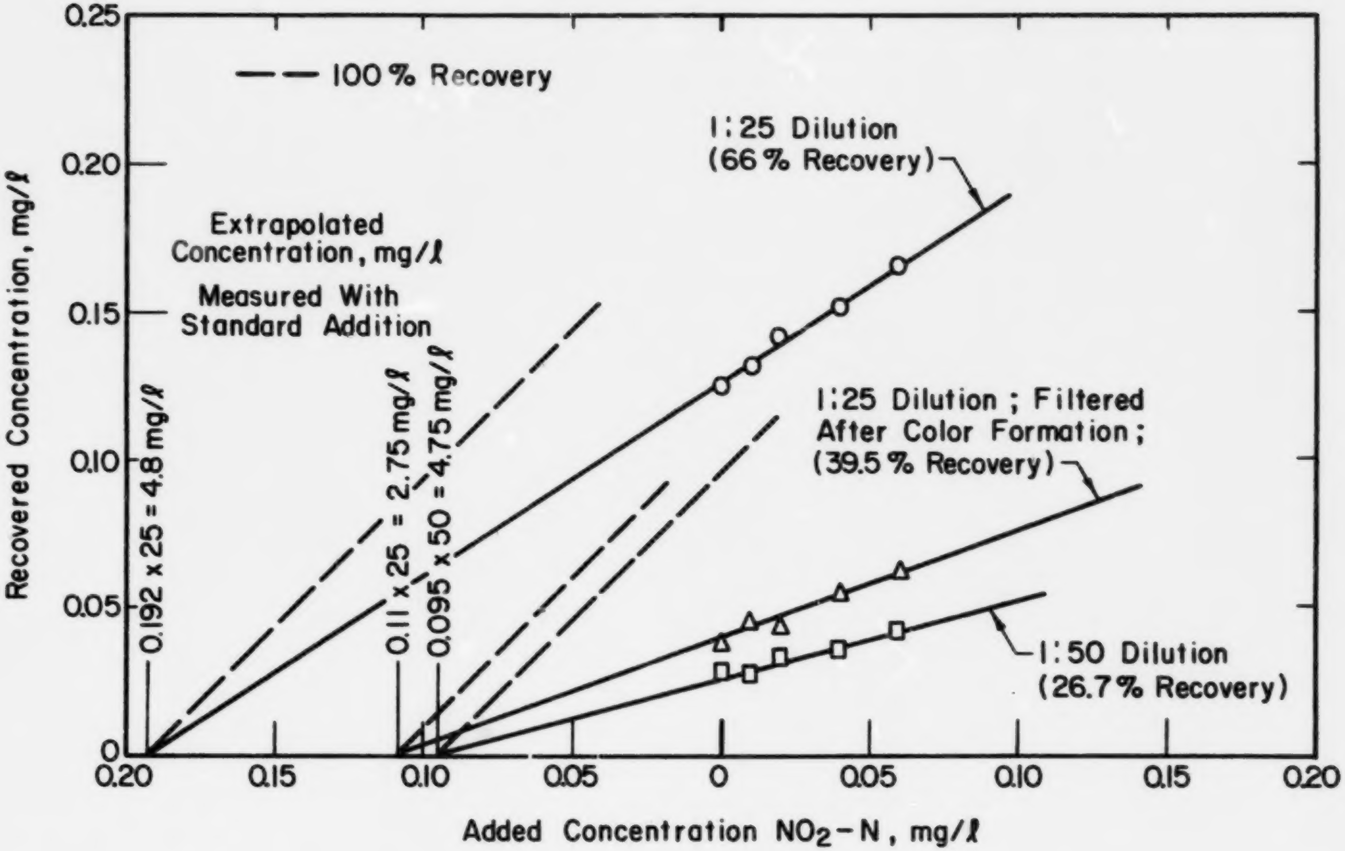

Figure 30. The Nitrite Determination with the Naphthylamine Method Using Standard Additions

## Reagents for the Naphthylethylenediamine Method

"EDTA solution: Dissolve 500 mg disodium ethylenediamine tetraacetate dihydrate in nitrite-free water and dilute to 100 mℓ.

Sulfanilic acid reagent: Completely dissolve 600 mg sulfanilic acid in 70 m hot distilled water, cool, add 20 mℓ conc. HCl, dilute to 100 mℓ with distilled water, and mix thoroughly.

Naphthylethylenediamine dihydrochloride reagent: Dissolve 800 mg of n-(1-napthyl) ethylenediamine dihydrochloride in distilled water to which 1.0 mℓ conc. HCl has been added. Dilute to 100 mℓ with distilled water and mix thoroughly.

Sodium acetate buffer solution, 2 M: Dissolve 16.4 g $NaC_2H_3O_2$ or 27.2 g $NaC_2H_3O_2 \cdot 3H_2O$ in nitrite-free water and dilute to 100 mℓ. Filter if necessary.

Stock nitrite solution: The reagent grade of sodium nitrite available commercially assays at less than 99 percent. Since nitrite is readily oxidized in the presence of moisture, fresh bottles of reagent are desirable for the preparation of the stock solution. The preferred approach is to determine the sodium nitrite content immediately before preparation of the stock solution and to keep bottles tightly stoppered against the free access of air when not in use. The sodium nitrite content may be determined by adding an excess of standard potassium permanganate solution, discharging the permanganate color with a standard reductant such as sodium oxalate or ferrous ammonium sulfate solution, and finally back-titrating with standard permanganate solution.

Preparation of Stock Solution: Dissolve 1.232 g sodium nitrite, $NaNO_2$, in nitrite-free water and dilute to 1,000 mℓ; 1.00 mℓ = 250μg N. Preserve with 1 mℓ chloroform.

Standard nitrite solution: Dilute 10.00 m intermediate nitrite solution to 1,000 mℓ with nitrite-free water; 1.00 mℓ = 0.500 μg N. Prepare daily.

Calcium hydroxide suspension: Prepare a 1 percent stock solution by dissolving 10 g CaO in 1 ℓ distilled water." (Standard Methods, 13th Ed., 1971, p. 241).

## Procedure for the Naphthylamine Method

Suspended solids are only partially removed by filtration, while better removal is obtained at a massive lime dosage of 5000 to 10,000 mg/ℓ $Ca(OH)_2$.

"Color Development: To 50.0 mℓ clear sample which has been neutralized to pH 7, or to an aliquot diluted to 50.0 mℓ, add 1.0 mℓ EDTA solution and 1.0 mℓ sulfanilic acid reagent. Mix thoroughly. At this point, the pH of the solution should be about 1.4. After the reaction has proceeded for 3 to 10 min, add 1.0 mℓ naphthylamine hydrochloride reagent and 1.0 mℓ sodium acetate buffer solution; mix well.

At this point, the pH of the solution should be 2.0. Measure the reddish purple color after 10 to 30 min. Measure the absorbance at or near 520 nm against a reagent blank and run parallel checks frequently against known nitrite standards, preferably in the nitrogen range of the samples.

$$\text{mg}/\ell \text{ nitrite N} = \frac{\mu\text{g nitrite N}}{\text{m}\ell \text{ sample}}$$

(Standard Methods, 13th Ed., 1971, p. 242-243).

## 8.7 THE AMMONIA DETERMINATION

### Principle

Ammonia is present in relatively high concentrations in young leachate due to the degradation of the organic nitrogen compounds. In more stabilized leachate it is present at lower concentrations since a significant portion has been converted to nitrates.

The oldest method to determine ammonia concentrations is the Nesslerization Method in which mercuric iodide and potassium iodide react with ammonia to give a yellow to brown color. Since this is identical to the color of the leachate, interferences may be encountered. Precipitates of calcium bicarbonate and ferric hydroxide also strongly interfere as do organic compounds such as aldehydes which makes the method less applicable to leachate analysis.

The phenate method as listed in Standard Methods to determine ammonia is based on the intense blue colored indophenol complex formed by the reaction of the ammonia hypochlorite and phenol catalyzed by a manganous salt, but color and turbidity, as are generally present in leachate, interfere with the analysis (APHA, 1971). The EPA (1974) automated procedure also uses the color reaction of ammonia with alkaline phenol hypochlorite to form the blue-green indophenol color (Berthelot Reaction). The interference by high concentrations of Ca and Mg may be partially reduced by the addition of EDTA or Rochelle salt. The presence of iron and chromium tends to enhance the color. The test is also markedly interfered with by the buffering capacity of leachate as a result of the high acidity. As the color of the reaction product is pH dependent, the standard used to calibrate the autoanalyzer should therefore have the same pH as the sample.

The most applicable method for leachate analysis consists of distillation of the ammonia in a phosphate buffer at pH 7.4 and collecting the distillate in boric acid. The ammonia can then be determined colorimetrically with the Nessler reagent when low concentrations are present, or by titration with a standard solution of strong acid at higher ammonia concentrations.

The selective ion electrode method as recommended by EPA (1974) is also free of many interferences mentioned above for the other methods.

### Interferences

The largest difficulty in the distillation step is maintaining the pH of 7.4. When the pH of the distillation mixture is too high, certain organic nitrogen compounds are converted to ammonia thus increasing the apparent concentration, and when the pH is too low, the recovery of ammonia is too low. A relatively large amount of Ca will decrease the pH since calcium and the phosphate buffer reacts to precipitate calcium phosphate, releasing hydrogen ions, and thus reducing the pH.

### Previous Studies

The interferences in the direct Nesslerization were recognized by Foree and Cook (1972) who therefore used the distillation step prior to the Nesslerization. Foaming may sometimes pose a problem in the distillation step. The EPA (1974) recommends distillation in borate buffer at a pH of 9.5 as opposed to 7.4 in *Standard Methods*. The former method was used by the State Water Quality Control Board of California (Appendix A). The automated indophenol method was used by Pohland and the Department of Environmental Resources of Pennsylvania (Appendix A). Since relatively little interference was reported for both the specific ion electrode and the Kjeldahl distillation, both were evaluated.

### Evaluation of Method

The ammonia concentration was tested with both the electrode and the distillation method. A calibration curve was made for the electrode with $NH_4Cl$ as a standard (Figure 31) whereafter the samples were run at a 1:10 and 1:50 dilution with standard amounts of $NH_4Cl$ added to the sample. The potentiometric method generally gave good results. Figure 32 shows that the extrapolated values at the 1:10 and 1:50 dilution are 570 mg/ℓ and 600 mg/ℓ respectively which is within 97 percent of each other. The 1:10 dilution gave a 113 percent recovery, slightly more than 100 percent, indicating that there are substances present in leachate that enhance the reading of the electrode. Samples should therefore be run at a sufficiently large dilution to eliminate this.

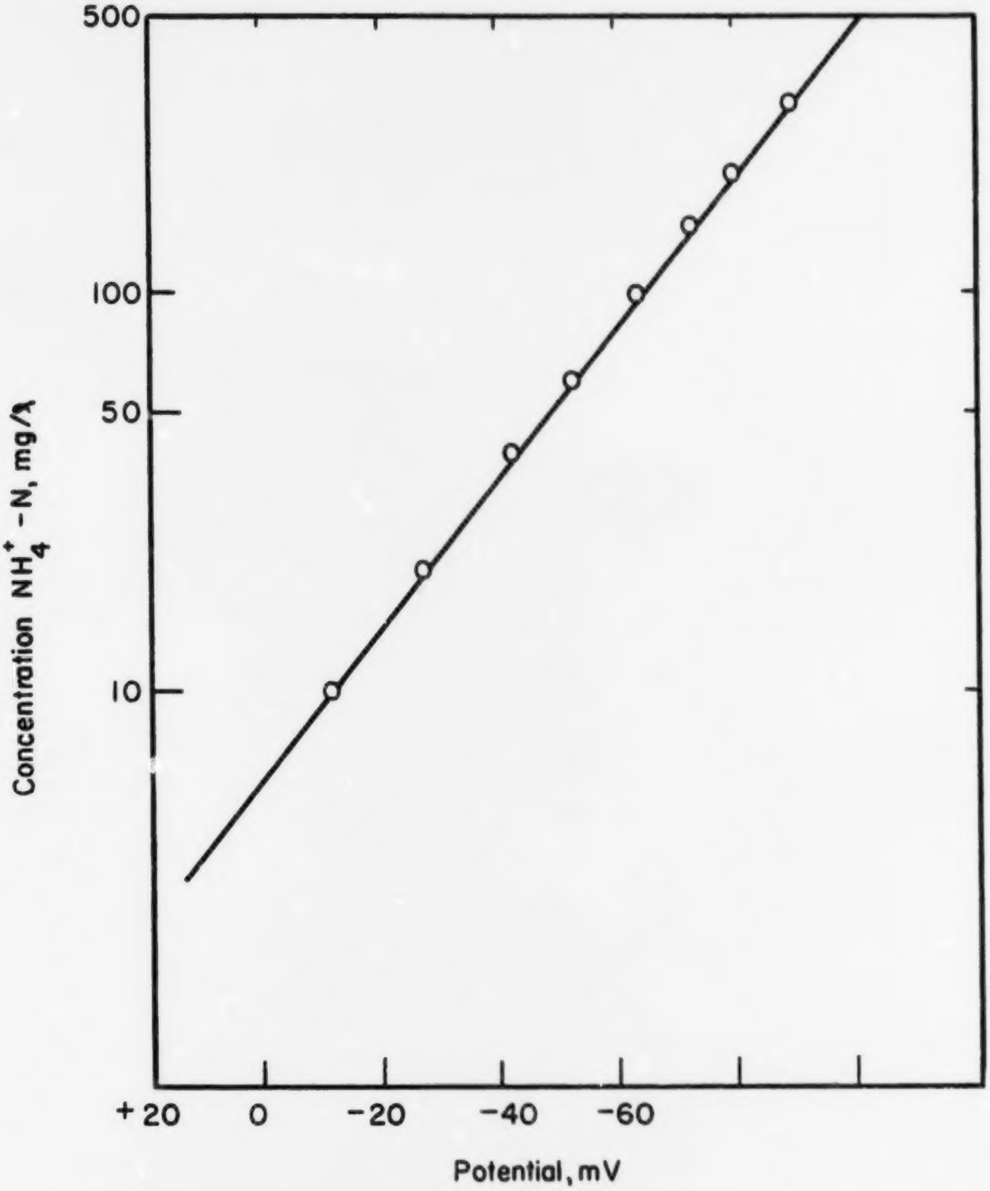

Figure 31. Calibration Curve for the Ammonia Electrode

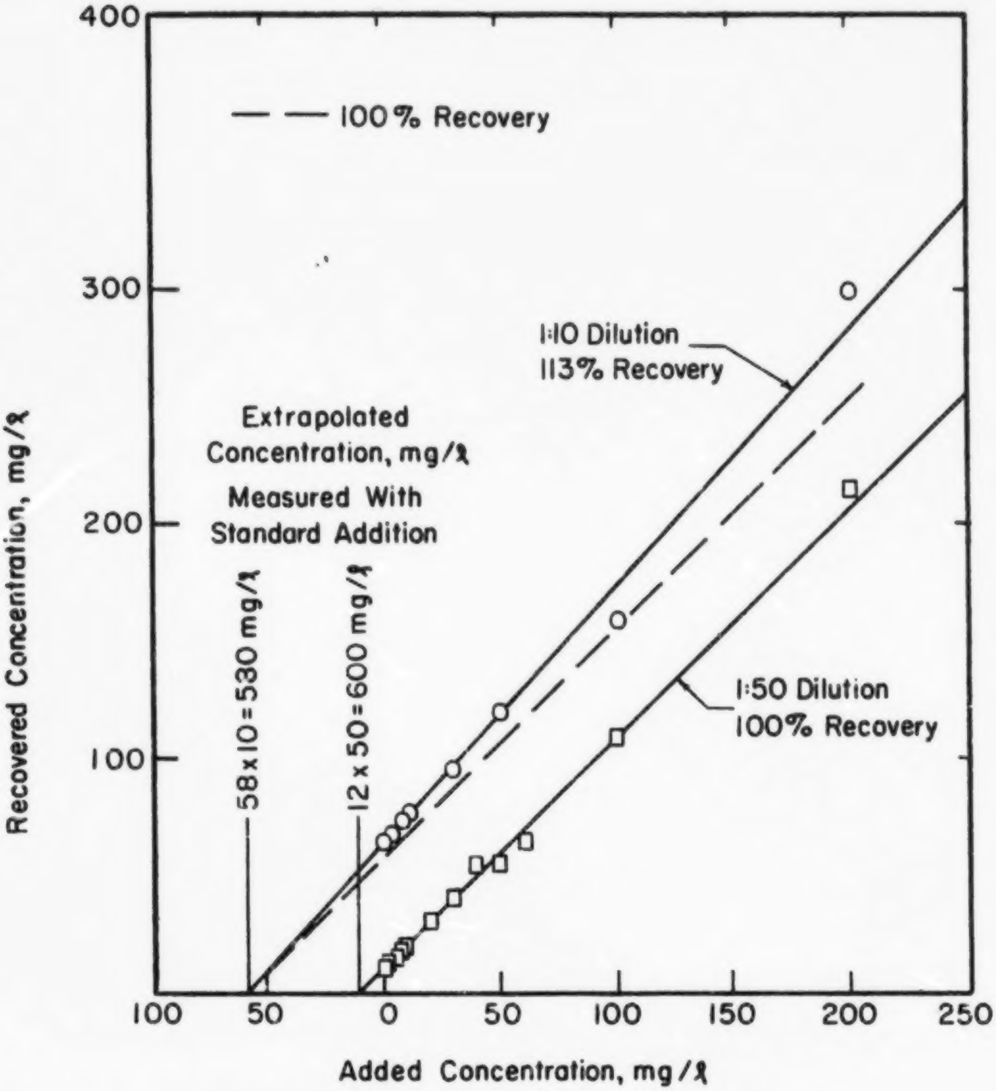

Figure 32. The Ammonia Determination with the Potentiometric Method Using Standard Additions

The distillation procedure gave similar results as the electrode for the 1:50 dilution i.e. 600 mg/ℓ with an almost 100 percent recovery at concentration below 75 mg/ℓ (Figure 33). The 1:10 dilution, however, gave a result of 720 mg/ℓ which is 20 percent higher than observed for the 1:50 dilution while the recovery was only 86 percent. Since this is an unsatisfactory response of the test, a further evaluation was made. A study of the literature showed that in order to obtain good ammonia recovery, the pH of the distillate should remain above 7.1 during the entire distillation. The pH is maintained at this level by addition of 10 mℓ buffer or 10 mℓ more for each 250 mg/ℓ Ca in the sample. In the 1:10 dilution this represents 10 + 10 = 20 mℓ and 15 mℓ for the 1:50 dilution. Measurement of the pH before and after distillation showed that the recommended amount of buffer could not maintain the pH at the desired level. The result of the pH decrease on the recovery of $NH_4^+$-N in the 1:50 dilution is shown in Figure 34. These data indicate that a decreasing pH causes a decreasing recovery of the ammonia. Figure 34 also shows that the pH decrease is dependent on the dilution of the leachate and is less significant at smaller dilutions possibly corresponding with higher buffer concentrations. However, when the final pH of the distillate becomes larger than 7.1 in the 1:50 dilution of 7.2 in the 1:10 dilution, the recovery exceeds 100 percent indicating that at higher pH nitrogeneous compounds are converted to ammonia and also distilled off. Further evaluation of the data shown in Figure 34 also indicated that increasing ammonia concentrations correspond to a decreasing pH. This then explains why the recovery of the ammonia in the 1:50 diluted leachate sample approaches 100 percent at low values but becomes less than 100 at increasing concentrations. Thus the ammonia concentration in the 500 mℓ sample should not exceed 75 mg/ℓ unless additional buffer is added. The results clearly show that the sample should not be distilled at pH 9.5 as recommended by EPA (1974) as nitrogeneous compounds will be hydrolyzed at that pH.

## Recommendations

It is recommended that ammonia concentrations be determined with either the specific ion electrode after sufficient dilution to reduce matrix interference of the leachate, or with the distillation method when the concentration in the diluted sample does not exceed 75 mg/ℓ unless additional buffer is added to the leachate sample. A pH maintained at 7.4 is sufficiently high to distill off the ammonia. A pH of 9.4 as recommended by EPA (1974) is too high, causing partial destruction of the organic nitrogen.

## Reagents for Ammonia Distillation and Titration Method

"Ammonia-free water: Prepare by ion-exchange or distillation methods. Since it is virtually impossible to store ammonia-free water in the lab-

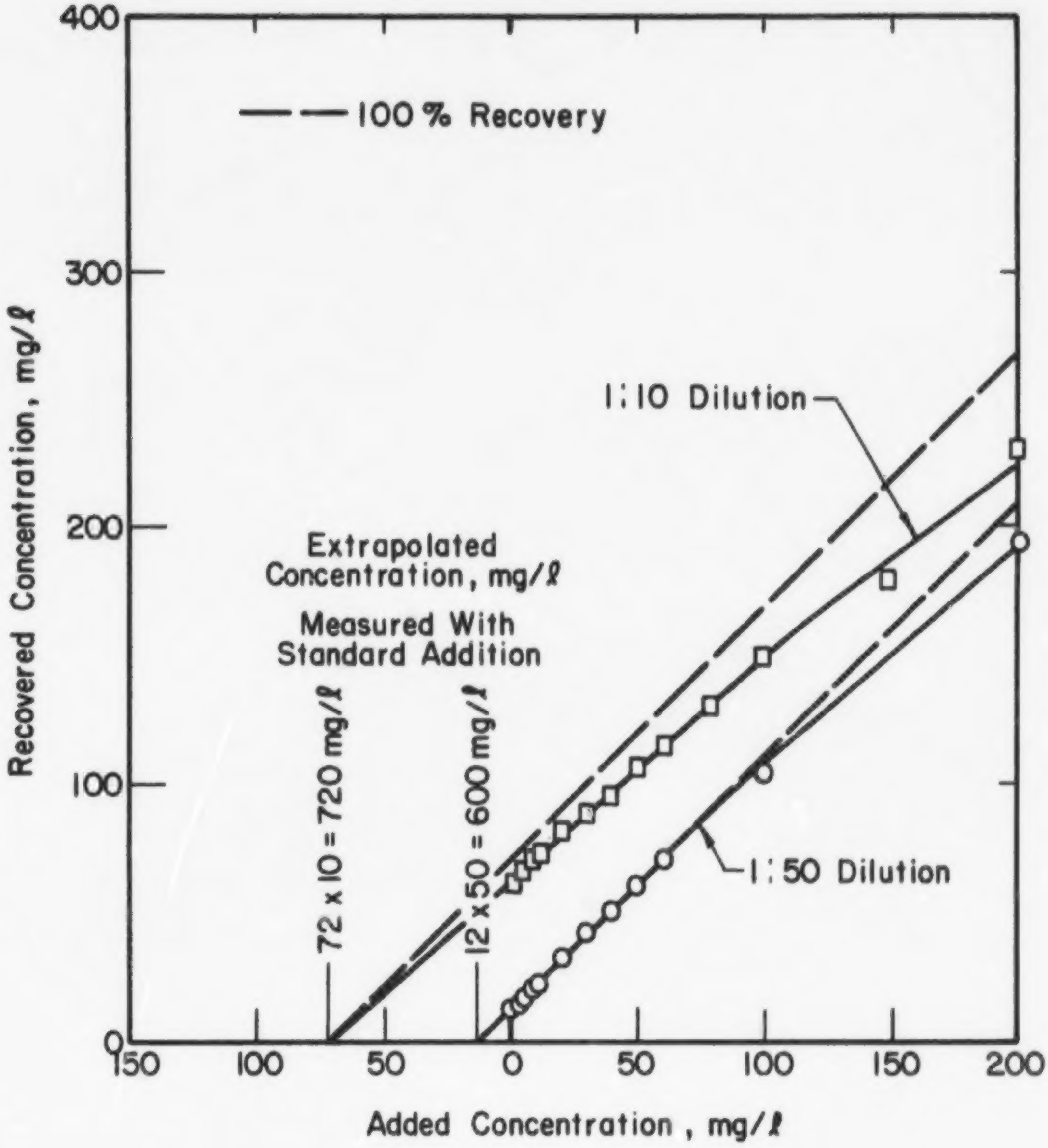

Figure 33. The Ammonia Determination with the Distillation Method Using Standard Additions

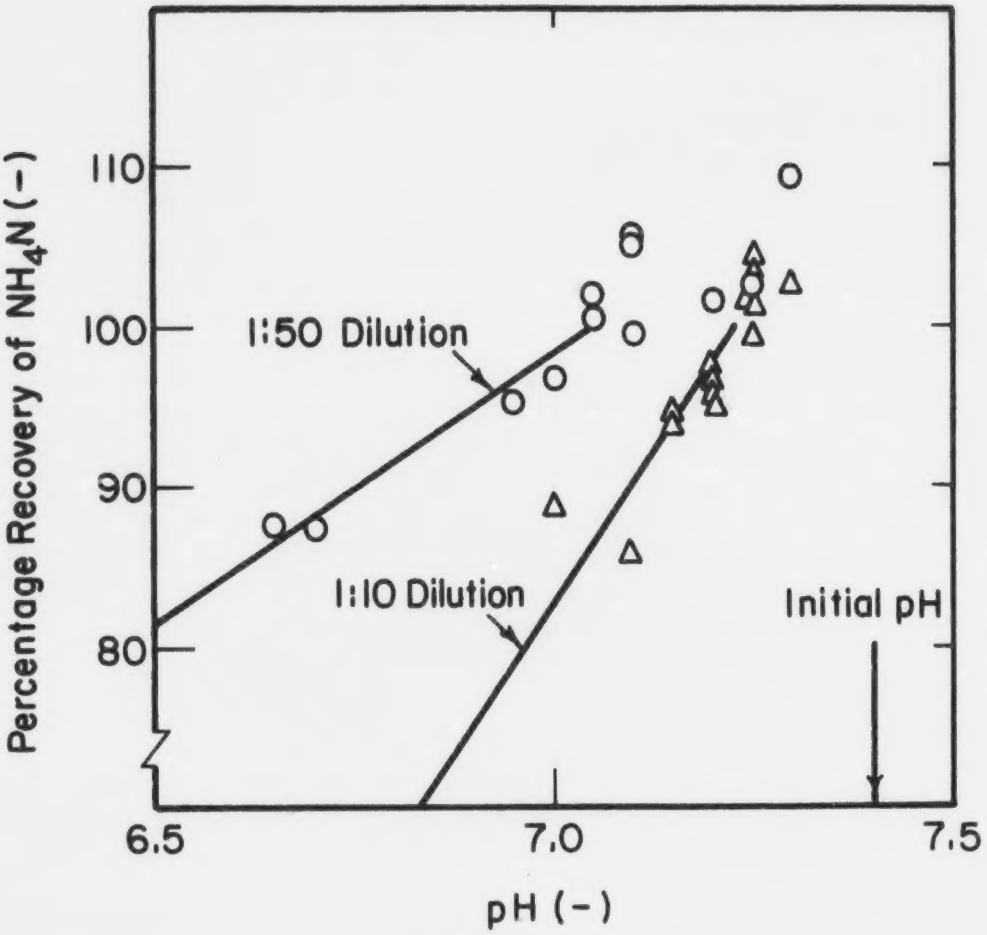

Figure 34. Effect of Final pH of Distillate on Recovery of Ammonia during the Kjeldahl Distillation

oratory without contamination from ammonia fumes, for best results prepare fresh for each batch of samples.

Phosphate buffer solution pH 7.4: Dissolve 14.3 g potassium dihydrogen phosphate, $KH_2PO_4$, and 68.8 g dipotassium hydrogen phosphate, $K_2HPO_4$, then dilute to 1 ℓ with ammonia-free water. Determine the ammonia nitrogen blank on the buffer solution." (Standard Methods, 13th Ed., 1971, p. 225).

"Mixed indicator solution: Dissolve 200 mg methyl red indicator in 100 mℓ 95 percent ethyl or isopropyl alcohol. Dissolve 100 mg methylene blue in 50 mℓ 95 percent ethyl or isopropyl alcohol. Combine the two solutions. Prepare monthly.

Indicating boric acid solution: Dissolve 20 g $H_3BO_3$ in ammonia-free distilled water, add 10 mℓ mixed indicator solution, and dilute to 1 ℓ. Prepare monthly.

Standard sulfuric acid titrant, 0.02 N: Prepare and standardize as directed in Alkalinity, Section 8.4. For greatest accuracy, standardize the titrant against an amount of sodium carbonate which has been incorporated in the indicating boric acid solution to reproduce the actual conditions of the sample titration. A standard acid solution, exactly 0.0200 N, is equivalent to 280 μg N per 1.00 mℓ." (Standard Methods, 13th Ed., 1971, p. 245).

## Procedures for Ammonia Distillation and Titration Method

"Sample preparation: Use a 500 mℓ sample or an aliquot diluted to 500 mℓ with ammonia-free water in order to obtain an ammonia concentration less than 75 mg/ℓ. If necessary, neutralize the sample to approximately pH 7 with the dilute acid or base, using a pH meter. Add 10 mℓ phosphate buffer solution. For most water samples this volume is sufficient to maintain a pH of 7.4 ± 0.2 during distillation. For samples containing more than 250 mg Ca, add an additional 10 mℓ buffer solution for each 250 mg Ca in the sample and adjust to pH 7.4 with acid or base.

Carry out the following steps without any intervening delay:

Preparation of equipment: Add 500 mℓ distilled water, 10 mℓ phosphate buffer solution, and a few glass beads or boiling chips to a flask of appropriate capacity; steam out the entire distillation apparatus until the distillate shows no trace of ammonia.

Distillation: In order to minimize contamination, leave the entire distillation apparatus assembled after the steaming-out process until just before the actual sample distillation is to be started. Empty the distilling flask, taking care to leave the glass beads or boiling chips in it. Pour in the neutralized and buffered sample. Distill at a rate of 6-10 mℓ/min with the tip of the delivery tube submerged, collecting the distillate in a 500-mℓ erlenmeyer flask containing 50 mℓ boric acid absorbent. Use additional 50-mℓ increments of boric acid for each mg of ammonia nitrogen distilled. Collect at least 300 mℓ distillate. Lower the collected distillate, free of contact with the delivery tube, and continue distillation during the last minute or two to cleanse the condenser and delivery tube. Dilute to 500 mℓ with ammonia-free water.

Titrate the ammonia in the distillate with standard 0.02 N sulfuric acid titrant until the indicator turns a pale lavender.

Blank: Carry a blank through all the steps of the procedure and apply the necessary correction to the results.

$$\text{mg}/\ell \text{ organic N} = \frac{(D-E) \times 280}{\text{m}\ell \text{ sample}}$$

where D = mℓ $H_2SO_4$ titration for sample and E = mℓ $H_2SO_4$ titration for blank." (Standard Methods, 13th Ed., 1971, pp. 246-247).

## 8.8 THE SODIUM AND POTASSIUM DETERMINATION

### Principle

Sodium (Na) and potassium (K) are present in high concentrations in leachate collected from a recently generating fill and retains relatively high concentrations with respect to the other cations during stabilization of the fill. Passage through soil may reduce the sodium and potassium concentration by exchange against calcium and magnesium.

The most rapid and sensitive method uses flame emission photometry to determine sodium and potassium concentrations at a wavelength of 5890 Å and 7665 Å. The sample is sprayed into a gas flame and excitation is carried out under carefully controlled conditions after which the intensity of light is measured by a potentiometric photometer.

### Interferences

Particulate matter can cause burner clogging and should be removed by filtration through a medium pore sized filter paper (APHA, 1971).

Potassium and calcium have been reported to interfere with the sodium determination if the potassium to sodium ratio is equal or larger than 5:1, or when the calcium to sodium ratio is equal to larger than 10:1. Among the common anions causing radiation interference are phosphates,chlorides, sulfates and bicarbonates, respectively,in relatively large amounts.

Indirect interferences are caused by changes in temperature and composition of the flame which results in a shift of equilibrium between gaseous atoms, ions or molecules. A low temperature flame is therefore recommended for sodium and potassium as it reduces the ionization of the atom. Recommended flames are the propane-air flame which has a temperature of approximately 1900° C, while higher temperatures of approximately 2400° C are obtained with an acetylene-air flame (Rich, 1965).

## Previous Studies

Most studies used flame emission photometry to determine Na and K concentration, and applied the method without modification. One study calculated Na and K concentrations from the hardness and total solid determinations. Only one study added Cs to the sample to suppress the ionization of the analytical ion.

Standard Methods recommends both the use of direct reading flame photometers, in which the light of the selected wavelength causes a current, and internal standard flame photometers, in which one cell intercepts the radiation emitted by the internal standard Li while the other cell intercepts the radiation of the element to be determined. The latter system is subject to fewer interferences then the former.

The EPA (1974) recommends atomic absorption spectroscopy to determine sodium and potassium at 3302 Å and 7665 Å, respectively, while the USGS (Brown et al., 1973) recommends a wavelength of 5888 Å and 7665 Å for sodium and potassium, respectively. For more sensitive determinations, EPA (1974) recommends a wavelength of 5890 Å for the sodium determination; a similar recommendation was made by Parker (1972). The EPA (1974) does not recommend any additions for the sodium and potassium determination, while Parker (1972) recommends a 1000 mg/l cesium nitrate addition for the sodium and potassium determination to suppress the ionization of the analyte ion, especially when using an air acetylene flame.

## Evaluation of the Method

An extensive evaluation of the method showed the necessity to add the easily ionizable ion Cs to the sample at a concentration of 1000 mg/l in the final dilution to suppress the ionization of the analytic ion.

## Recommendations

It is recommended that Na and K be determined by flame photometry and that Cs is added to the sample to suppress the ionization of the analyte ion in the flame,when the determination is made by atomic absorption spectroscopy.

### Reagents for the Sodium Determination

Deionized distilled water: Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

Stock sodium solution: Dissolve 2.542 g $NaCl$ dried at 140° C and dilute to 1,000 mℓ with deionized distilled water to form a solution containing 1.00 mg Na per 1.00 mℓ.

Intermediate sodium solution: Dilute 10.00 mℓ stock solution with deionized distilled water to 100.0 mℓ to form a solution containing 100 µg Na per 1.00 mℓ. Use this intermediate solution for preparing the calibration curve in the sodium range of 1-10 mg/ℓ." (Standard Methods, 13th Ed., 1971, p. 318). Store all solutions in polyethylene bottles.

Prepare a $CsNO_3$ stock solution: Dissolve 14.7 g dried at 104° C and dilute to 100 mℓ with deionized distilled water to form a solution containing 10,000 mg/ℓ Cs.

### Procedure for the Sodium Determination

Pipet 10 mℓ of the Cs stock solution and add to 50 mℓ of filtered sample, dilute to 100 mℓ.

Instrument operation: Because the differences between the makes and models of satisfactory flame photometers render impossible the formulation of detailed instructions applicable to every instrument, follow the manufacturer's recommendation for the selection of the proper photocell and wavelength, the adjustment of the slit width and sensitivity, the appropriate fuel and air or oxygen pressures, and the steps for warm-up, correcting for flame background, rinsing of the burner, ignition of sample, and measurement of emission intensity. Because of the relative high concentrations of sodium in leachate a wavelength of 3302 Å will be sufficient for the desired accuracy.

### Reagents for the Potassium Determination

"Deionized distilled water: Use this water for the preparation of all reagents, calibration standards, and as dilution water.

Stock potassium solution: Dissolve 1.907 g potassium chloride, $KCl$ dried at 110° C and dilute to 1,000 mℓ with deionized distilled water to form a solution containing 1.00 mg K/1.00 mℓ.

Intermediate potassium solution: Dilute 10.00 mℓ stock potassium solution with deionized distilled water to 100 mℓ to make a solution containing 100 µg K/1.00 mℓ. Use this solution for preparing the calibration curve in the potassium range of 1-10 mg/ℓ." Store all solutions in polyethylene bottles.

Prepare a $CsNO_3$ stock solution Dissolve 14.7 g dried at 104° C and dilute to 1000 mℓ with deionized distilled water to form a solution containing 10,000 mg/ℓ Cs." (Standard Methods, 13th Ed., 1971, p. 284).

### Procedure for the Potassium Determination

Pipet 10 mℓ of the Cs stock solution and add to 50 mℓ of filtered sample, dilute to 100 mℓ.

"Instrument operation: Because the differences between the makes and models of satisfactory flame photometers render impossible the formulation of detailed instructions applicable to every instrument, follow the manufacturer's recommendation for the selection of the proper photocell and wavelength, the adjustment of the slit width and sensitivity, the appropriate fuel and air or oxygen pressures, and the steps for warm-up, correcting for flame background, rinsing of the burner, ignition of sample, and measurement of emission intensity. A wavelength of 7665 Å is recommended for most measurements but may be changed to 4044 Å when very high concentrations are present." (Standard Methods, 13th Ed., 1971, p. 319).

## 8.9 THE Ca AND Mg DETERMINATION

### Principle

Calcium (Ca) can be determined gravimetrically as calcium oxalate, with the permanganate titrimetric method, the EDTA titrimetric method or by atomic absorption spectroscopy. The gravimetric method which measures the precipitate of calcium oxalate at alkaline pH is interfered by iron, phosphate and suspended matter, all present in leachate since these substances are also removed by filtration. In the permanganate titrimetric method the precipitated calcium oxalate is redissolved in acid and titrated with permanganate which oxidizes the oxalate. This method is therefore subject to the same interferences as the gravimetric method. In the EDTA titrimetric method the magnesium (Mg) is first precipitated at high pH after which EDTA is added to combine with the Ca. A color indicator is used to indicate the endpoint of the titration when all Ca is complexed. The method is subjected to numerous interferences and 20 mg/ℓ of both ferrous and ferric iron interfere, as do 5 mg/ℓ zinc, 5 mg/ℓ lead, 2 mg/ℓ copper while an alkalinity above 20 mg/ℓ causes an indistinct endpoint. Due to the limitations of the previous methods, the EPA (1974) recommends atomic absorption spectroscopy as the most accurate measurement subject to least interferences.

Magnesium can be determined by the gravimetric method only after prior removal of Ca and is generally determined in the filtrate of the Ca gravimetric method. In the gravimetric Mg method diammonium hydrogen phosphate precipitates Mg as magnesium ammonium phosphate in an ammoniacal solution. Iron and suspended matter however interfere. Magnesium can also be determined with the photometric method in which magnesium hydroxide is precipitated in the presence of brilliant yellow. Chlorides at 250 mg/ℓ, iron at 2.5 mg/ℓ and any zinc, however, interfere, making the method less suitable for leachate analysis. For that reason the EPA (1974) recommends the atomic absorption method.

### Interferences

Phosphate and sulfate interferes in the atomic absorption calcium determination and 200 mg/ℓ of each caused a 35 percent and a 30 percent depression,respectively (Parker, 1972). Both effects are masked by the addition of Lanthanum chloride. Concentrations of more than 1000 mg/ℓ magnesium and 500 mg/ℓ each of sodium and potassium cause a 5-10 percent enhancement due to suppression of the calcium ionization (Brown *et al.*, 1970). The magnesium determination is interfered with by more than 400 mg/ℓ each of sodium, potassium and calcium, while phosphates and sulfates also cause interferences. Silicates and carbonates at 200 mg/ℓ each caused a 42 percent and 17 percent depression respectively (Parker, 1972). Phosphate for example will bind the magnesium and prevent the magnesium atomic absorption when the light passes through the flame. Interferences in the calcium and magnesium determinations are reduced by addition of an inorganic "releasing" agent La to the sample which prevents the binding of Ca and Mg by anions. The interferences are also reduced by using a nitrous oxide-acetylene flame, instead of the lower temperature air-acetylene flame.

### Previous Studies

Most of the early studies measuring calcium and magnesium in leachate use colorimetric analysis, but later studies generally use EDTA titration. Only recent studies, however, use atomic absorption spectroscopy. In most of these studies, La is added as a releasing agent to the sample.

The *Standard Methods* recommend a wavelength of 2852 Å for the magnesium determinations. Brown *et al.* (1970) uses 4227 Å for calcium and 2852 Å for magnesium. The EPA (1974) recommends 4227 Å for most calcium measurements, 2399 Å only for very high calcium concentrations and 2852 Å for magnesium. The EPA (1974) recommends a final concentration of 4500 mg/ℓ La while all other studies recommend 10,000 mg/ℓ in the final dilution.

### Evaluation of Method

Evaluation showed that only 90 percent of the added Ca is recovered from leachate samples but that approximately 100 percent was recovered in the presence of La. The Mg recovery in the presence of La did not differ greatly from the recovery in the absence of La.

### Recommendations

It is recommended that Ca and Mg be determined with atomic absorption spectroscopy using 10,000 mg/ℓ La to reduce interferences.

### Reagents for the Calcium Determination

"Stock lanthanum reagent: Dissolve 58.65 g lanthanum oxide, $La_2O_3$, in 250 mℓ conc. HCl. Dilute to 1,000 mℓ with distilled water to obtain a solution containing 5 g La/100 mℓ. Add the acid slowly until the material is dissolved. Add sufficient amounts of this solution to the standards and unknowns in order to obtain a final working concentratin of 1 g La/100 mℓ volume."

Stock calcium solution: Suspend 1,250 g $CaCO_3$, analytical reagent grade, dried at 180° C for 1 hour before weighing in deionized distilled water and dissolve cautiously with a minimum of dilute HCl, dilute to 1,000 mℓ with deionized distilled water; 1 mℓ = 0.5 mg/ℓ or 500 mg/ℓ.

Prepare dilutions of the stock calcium solutions to be used as calibration standards. To each standard add 2 mℓ La stock solution and dilute till 10 mℓ.

### Procedures for Calcium Determination

When high concentrations of suspended solids are present, the sample will have to be digested according to 8.11, otherwise the Ca can be determined directly.

"Because the differences between makes and models of satisfactory atomic absorption spectrophotometers render impossible the formulation of detailed instructions applicable to every instrument, follow the manufacturer's operating instructions. As a rule, choose the correct hollow cathode lamp, install, and align in the instrument; position the monochromator at the correct wavelength indicated by EPA (1974); select the proper monochromator slit width; set the light source current according to the manufacturer's recommendation; light the flame and regulate the flow of fuel and oxidant; adjust the burner for maximum absorption and stability; and balance the photometer. Then run the standards needed for the working curves and plot the concentrations of the standards against absorbance. If necessary on some instruments, convert percentage absorption to absorbance (the calibration curves are nearly linear for most elements). Next, run the samples and read the concentration of each sample from the calibration curve. Overcome instrumental drift by conducting the absorbance measurements of blank, calibration standards, and samples frequently and without undue delay. Record multiple readings (three or more) for averaging." Some of the recommended instrumental parameters are: measurement with the Ca hollow cathode lamp at 4227 Å; use of air-acetylene fuel and a reducing type flame." (Standard Methods, 13th Ed., 1971, p. 213).

## Reagents for the Magnesium Determination

"Stock lanthanum reagent: Dissolve 58.65 g lanthanum oxide, $La_2O_3$, in 250 mℓ conc. HCl. Dilute to 1,000 mℓ with distilled water to obtain a solution containing 5 g La/100 mℓ. Add the acid slowly until the material is dissolved. Add sufficient amounts of this solution to the magnesium standards and unknowns in order to obtain a final working concentration of 1 g La/100 mℓ volume." (Standard Methods, 13th Ed., 1971, p. 212-213).

Stock magnesium solution: Dissolve 0.829 g of magnesium oxide, MgO in 10 mℓ of redistilled $HNO_3$ and dilute to 1 ℓ with deionized distilled water; 1 mℓ = 0.50 mg Mg, 500 mg/ℓ.

## Procedures for Magnesium Determination

Prepare dilutions of the stock calcium solution to be used as calibration standards. To each standard add 2 mℓ La stock solution and dilute till 10 mℓ.

Because the differences between makes and models of satisfactory atomic absorption spectrophotometers render impossible the formulation of detailed instructions applicable to every instrument, follow the manufacturer's operating instructions. As a rule, choose the correct hollow cathode lamp, install, and align in the instrument; position the monochromator at the correct wavelength indicated by EPA (1974); select the proper monochromator slit width; set the light source current according to the manufacturer's recommendation; light the flame and regulate the flow of fuel and oxidant; adjust the burner for maximum absorption and stability; and balance the photometer. Then run the standards needed for the working curves and plot the concentrations of the standards against absorbance. If necessary on some instruments, convert percentage absorption to absorbance (the calibration curves are nearly linear for most elements). Next, run the samples and read the concentration of each sample from the calibration curve. Overcome instrumental drift by conducting the absorbance measurements of blank, calibration standards, and samples frequently and without undue delay. Record multiple readings (three or more) for averaging. Some of the recommended instrumental parameters are: measurement with the Mg hollow cathode lamp at 2852 Å; use of air-acetylene fuel and a reducing type flame.

## 8.10 HARDNESS DETERMINATION

### Principle

The hardness reflects the total concentration of polyvalent metals mainly calcium and magnesium but will include iron, zinc and copper when present in significant quantities. The most accurate method is by summation of the individual polyvalent metals as measured by atomic absorption spectroscopy which are then expressed as $CaCO_3$ equivalents.

A more rapid method is based on EDTA titration of the sample. Addition of Eriochrome Black T (EBT) results in wine red color as a result of the interaction with Ca and Mg. Titration with EDTA will complex these metals after which the EBT color changes from wine red to blue. The EPA (1974) recommends calmagite as an indicator instead of EBT, which causes a color change from red to blue during the titration. The automated EPA (1974) method is based on the exchange of Mg in Mg-EDTA for other polyvalent cations, followed by colorimetric determination of Mg by calmagite to give a red complex.

### Interferences

Fading of the endpoint is caused by the interference of some heavy metals which can be reduced by addition of complexing agent such as NaCN (extremely toxic). However, even after addition of the NaCN, iron, copper or zinc at a concentration above 10 mg/ℓ will interfere and contribute to the hardness (Brown, et al., 1970). The EDTA methods as recommended by EPA (1974) are therefore subject to similar interferences. Suspended solids and organic matter will also interfere with the determination as they influence the chelation of the cations by EDTA, but can be removed by drying and ignition at 550° C.

### Previous Studies

Most studies use the EDTA titration for the hardness determination. Some of the studies add NaCN to the sample to reduce interferences from other metals. Only a few studies determine the hardness by calculation from the concentraiton of the individual components.

### Evaluation of the Method

Hughes et al. (1971) stated that the values for hardness as calculated from the analysis of the individual ions did not compare with the values obtained from the EDTA titration. Difficulty encountered in observing the exact endpoint of the titration was due to the presence of colored suspended matter. The County of Sonoma, Emcon Associates (1973) also noted that addition of NaCN did not reduce all interferences.

### Recommendations

It is recommended that the hardness be calculated from the concentration of the individual polyvalent metals as determined with atomic absorption spectroscopy and should include Ca, Mg, Fe, Al, Zn, Cu and other polyvalent cations.

## 8.11 DETERMINATION OF HEAVY METALS

### Principle

Although several colorimetric methods are available for heavy metal determinations all are subject to strong interferences. For that reason EPA (1974) recommends atomic absorption for the determination of most elements.

### Interferences

Several interferences are reported for the atomic absorption determination and can be classified as chemical, non-atomic, ionization and spectral (EPA, 1974). Chemical absorption occurs when heavy metals are not available in the atomic form because of molecular combination with anions present in the solution. This interference can sometimes be overcome by addition of a releasing agent such as Cs. The presence of a high concentration of dissolved solids may cause a non-atomic interference such as by light scattering. This effect is partially corrected by measuring absorbance of a nearby non-adsorbing wavelength. Ionization interferences occur when the atom ionizes in the flame after which it is not available for atomic absorption. This interference is reduced by addition of an easily ionized element such as Cs to suppress the ionization of the analyte atom. Spectral interference can occur when the absorbing wavelength of another element falls within the width of the absorption line of the analyte atom. Such interference is partially reduced by narrowing the slit width of instrument.

### Previous Studies

The first studies analyzing leachate use colorimetric analysis but later studies generally use atomic absorption methods. Some of these studies, however, continue to measure iron with colorimetric methods. One study removed turbidity from the sample by centrifugation (Fungaroli, 1971) but this may have reduced the heavy metal content in the sample since several metals are adsorbed onto the ferric hydroxide particles. The turbidity interference is best reduced by acid digestion as recommended by EPA (1974). None of the studies use the standard addition method to evaluate the recovery of the determination.

### Evaluation of the Method

An extensive study was made of the interferences of the atomic absorption method in leachate analysis and interferences were found to reduce the recovery by as much as 44 percent. The interferences were especially large for the elements Pb, Cu, Ni and Cr and smaller for Zn and Cd and was best noticeable in high strength leachate, but decreased in magnitude for more stabilized leachate. The broad non specific molecular absorption and light scattering is measured at a bordering wavelength or at the same wavelength as the analyte ion using an hydrogen lamp.

### Recommendations

It is recommended that the heavy metals be determined with atomic absorption techniques and that standard additions are used for leachates of high strength to determine the magnitude of the interference. The standard additions should be used for the elements lead, copper, nickel and chromium, but may be omitted for Zn and Cd. For total metal analysis the sample should be collected in a polyethylene bottle and acidified to pH 2 with 1:1 redistilled nitric acid. When the dissolved metals, i.e. filterable through 0.45 μ are determined, the suspended metals should be determined concurrently.

### Procedures for Total Metal Analysis

"Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 mℓ of conc. redistilled $HNO_3$. Place the beaker on a hot plate and evaporate to dryness cautiously, making certain that the sample does not boil. Cool the beaker and add another 3 mℓ portion of conc. redistilled $HNO_3$. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated by a light colored residue). Add sufficient distilled 1:1 HCl and again warm the beaker to dissolve the residue. Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis." (EPA, 1974, p. 83).

"Because the differences between makes and models of satisfactory atomic absorption spectrophotometers render impossible the formulation of detailed instructions applicable to every instrument, follow the manufacturer's operating instructions. As a rule, choose the correct hollow cathode lamp, install, and align in the instrument; position the monochromator at the correct wavelength indicated by EPA (1974); select the proper monochromator slit width; set the light source current according to the manufacturer's recommendation; light the flame and regulate the flow of fuel and oxidant; adjust the burner for maximum absorption and stability; and balance the photometer. Then run the standards needed for the working curves and plot the concentrations of the standards against absorbance. If necessary on some instruments, convert percentage absorption to absorbance (the calibration curves are nearly linear for most elements). Next, run the samples and read the concentration of each sample from the calibration curve. Overcome instrumental drift by conducting the absorbance measurements of blank, calibration standards, and samples frequently and without undue delay. Record multiple readings (three or more) for averaging." (Standard Methods, 13th Ed., 1971, p. 213).

The determination of arsenic and selenium by AA using the gaseous hydride method may not be satisfactory, since reduction to the trivalent form with $SnCl_2$ may not be complete. The conversion to gaseous arsine after addition of zinc metal may also not be complete. Colorimetric methods are therefore recommended. The analysis of mercury by AA with the cold vapor technique, also depends on the reduction of the sample with $SnSO_4$ or $SnCl_2$, which may not be complete when other oxidants in high concentrations are present.

# SECTION 9

# BIOLOGICAL PARAMETERS

The biological parameters indicate the presence and action of bacteria and as such should complement analysis of physical and chemical parameters in leachate. The biological properties of leachate should reflect the analysis of specific chemical constituents. Acid fermenting bacteria for example are expected to be found when the free volatile fatty acids experience high concentrations, while anaerobic methane fermenting bacteria are expected when free volatile fatty acids are decreasing in concentration in the leachate. Since the free volatile fatty acids are more biodegradable than other chemical components present in leachate the oxygen demand exerted by bacteria during aerobic decomposition of the substrate, a biological parameter, will parallel the concentration of free volatile fatty acids, a chemical parameter.

## 9.1 THE BOD DETERMINATION

### Principle

The Biochemical Oxygen Demand determination is a bioassay type procedure and measures the oxygen demand exerted by microorganisms during uptake of degradable substrates and by chemical oxidation reactions. The sample is incubated under aerobic conditions in the dark at 20° C during a five day period.

### Interferences

Relative low results are obtained with the test when toxic compounds are present that inhibit the bacterial population or when a biomass is used that is not adopted to the specific substrate.

### Previous Studies

In the early studies by Merz (1954) the leachate was seeded with settled sewage to establish an aerobic biomass. Later studies by Qasim (1965), Fungaroli (1971), and the EPA Solid and Hazardous Waste Research Laboratory (Appendix A) omitted this step. Recent studies, County of Sonoma, Emcon Associates, 1973; Foree and Cook, 1972; and Mao and Pohland, 1973, however, have included this step. Most studies ran the test for five days but Hughes et al. (1971) selected a 20 day incubation period possibly including a nitrification step, since his BOD values were sometimes larger than the COD values. The DO in the BOD bottles is generally determined with the Azide modification or using a electrometric DO probe.

The effect of omitting the seeding step in the BOD test to introduce aerobic bacteria was illusted by the data from Cook (1966). The study showed that the BOD/COD ratio was 0.095 for an anaerobic leachate sample collected within a landfill and 0.23 for a leachate sample generated under aerobic conditions collected at the outer edges of the fill. The two samples, however, had similar COD values and were equally biodegradable, since aeration at room temperature caused a 40 percent COD decrease after five days in both samples. The BOD values and the BOD/COD ratios should, therefore, be equal, but this was not observed since the anaerobic leachate sample was not seeded by aerobic bacteria. The effect of seed omission in the anaerobic sample was further illustrated in the cumulative oxygen uptake as measured with the Hach apparatus which only showed a significant increase after an eight day lag period, while the leachate sample generated under aerobic conditions and having an aerobic biomass showed such increase after only 4 days.

### Evaluation of the Method

Evaluation of the BOD test shows that the outcome of it is dependent on the dilution used. For example, Figure 35 shows that the undiluted leachate sample (NW-17) from an old fill in N. E. Illinois has a five-day oxygen demand of 4.5 mg/ℓ. The 5 day oxygen demand of the 0.19 mg/ℓ seed added to the test was 0.60 mg/ℓ. This results in an actual $BOD_5$ of 4.5 minus 0.60 is equal to 3.9 mg/ℓ. A BOD/COD ratio of 0.048 was obtained with this BOD value and the known COD of the sample. The 1:8 diluted sample, however, had a five-day oxygen demand of 3.72 mg/ℓ or a net $BOD_5$ (3.72-0.60=) 3.12 mg/ℓ. By converting this value on the basis of an undiluted sample, this would represent a $BOD_5$ of 25 mg/ℓ which is six times higher than measured with the undiluted sample. As no inhibitor was added, the oxygen demand in the diluted bottles may partially be due to nitrification.

This discrepancy in the outcome of the BOD test was not found when a high strength leachate sample was tested. Figure 36 shows that the calculated oxygen demand of the 1:1500 and 1:4000 dilution of the two seeded Sonoma samples are comparable, while the 1:2500 dilution gave a slightly higher value. The 1:500 dilution oxygen demand exceeded the dissolved oxygen present in the sample and therefore can not be used for the BOD calculation. The spread in BOD data is substantial, with the highest calculated BOD value 40 percent higher than the lowest one for the two samples. Since the organic matter is biodegradable, most of the oxygen demand is consumed within the first two days, while the period of 2 to 5 days is probably used to degrade excreted intermediates and stored intracellular materials. The rapid oxygen uptake also indicates that this leachate sample is rather treated by biological means than by physical-chemical processes. The leachate of the old fill, however, is not subject to rapid biological degradation and is preferably treated by physical chemical processes.

If a detailed approach, such as serial dilutions studied here, is not taken, the dilution factor at which the test was conducted should be stated clearly, since the uptake rate is concentration dependent as

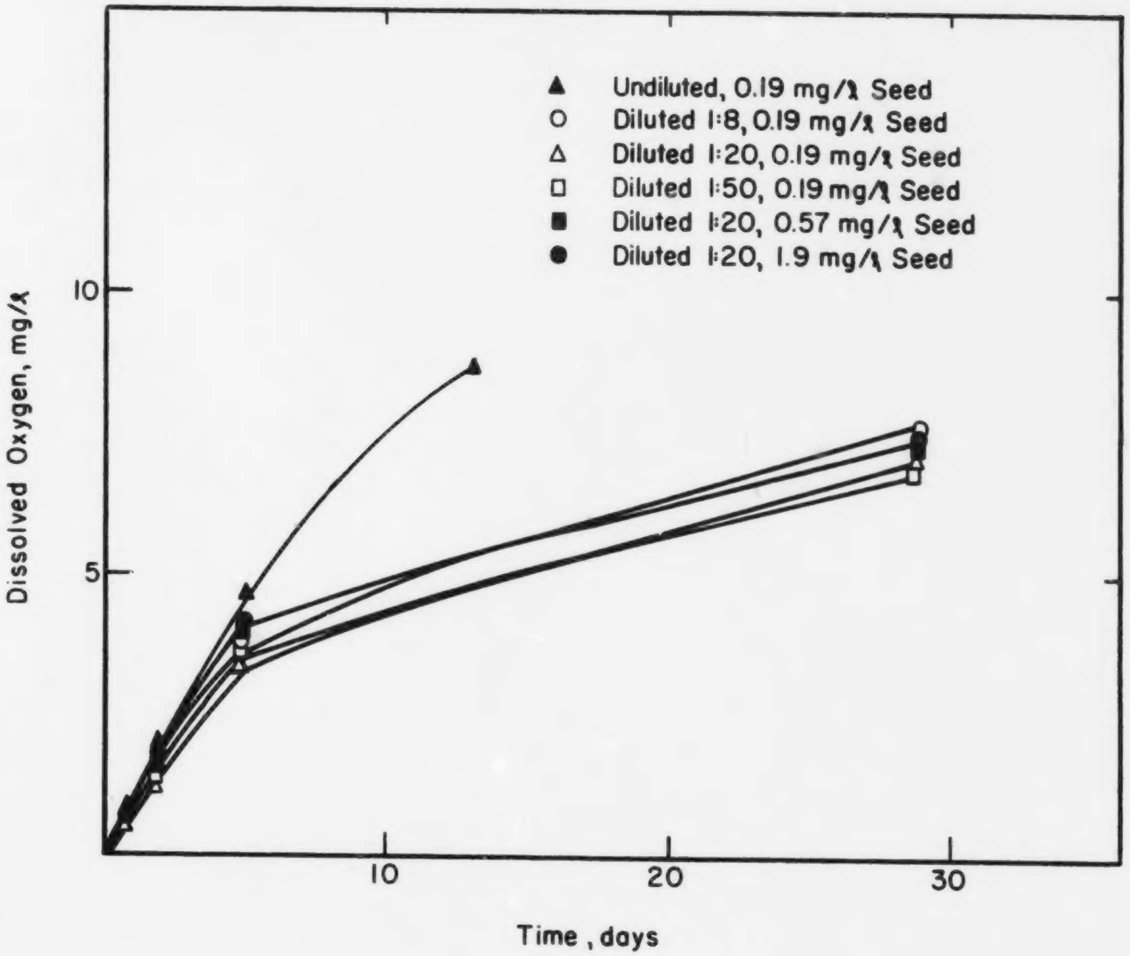

Figure 35. The DO Uptake as Affected by the Dilution Used, as Measured in a Biologically Stabilized Leachate

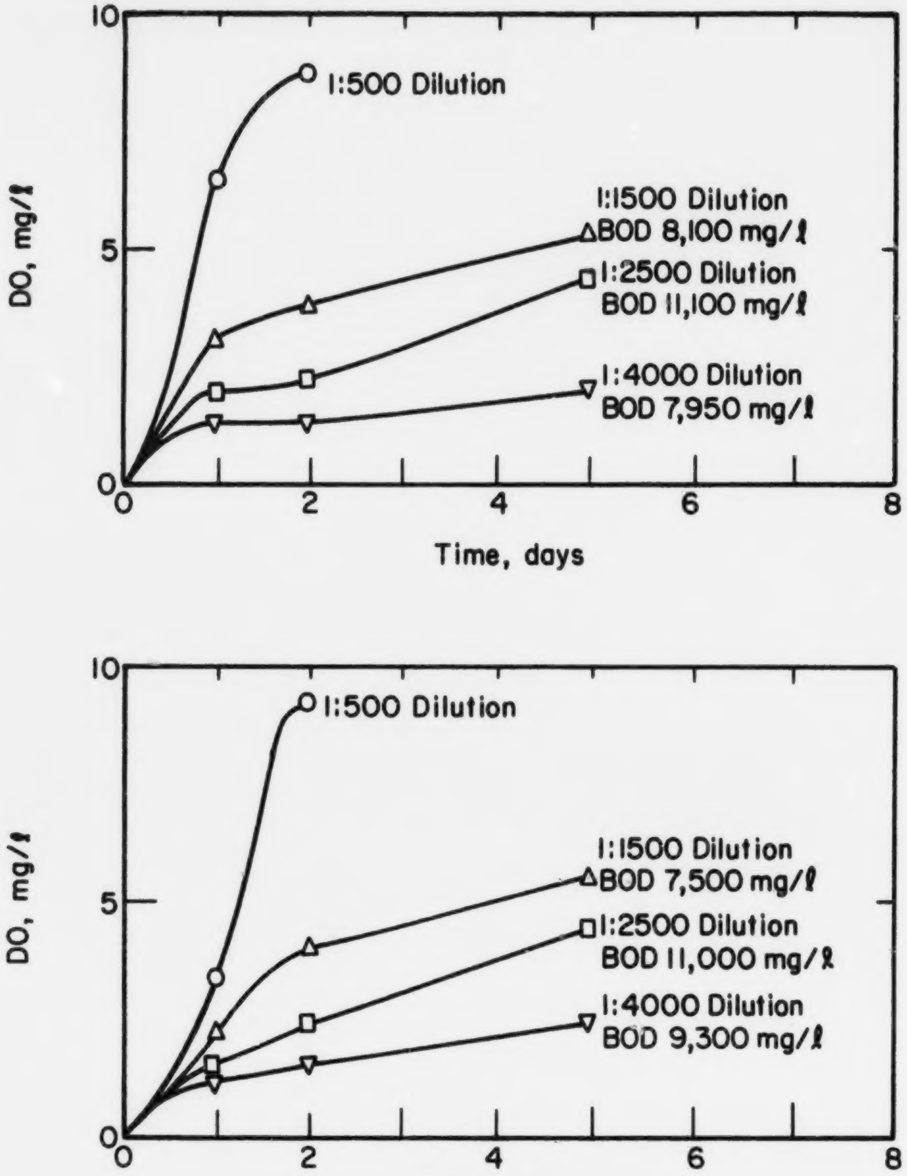

Figure 36. The DO Uptake as Affected by the Dilution Used, As Measured in a Leachate Sample from a Fill Recently Generating Leachate

generally expressed by Monod kinetics (Gaudy, 1972). It should be realized that the outcome of the test only gives an indication of the amount of biodegradable organic matter present in the diluted sample. More reliable and accurate parameters would be obtained by analyzing leachate for the specific biodegradable compounds, such as free volatile fatty acids, TOC removal of the leachate sample after batch activated sludge treatment, or expressing the BOD test in terms of Monod parameters.

### Recommendations

It is recommended that the BOD test be run according to Standard Methods and that the dilution water be seeded with settled sewage. BOD values obtained should be judged carefully and be determined parallel with comparable chemical tests such as free colatile fatty acids, COD or TOC.

### Reagents

"Distilled water: Water used for solutions and for preparation of dilution water must be of the highest quality, distilled from a block tin or all-glass still; it must contain less than 0.01 mg/ℓ copper and be free of chlorine, chloramines, caustic alkalinity, organic material or acids.

Phosphate buffer solution: Dissolve 8.5 g potassium dihydrogen phosphate, $KH_2PO_4$, 71.75 g dipotassium hydrogen phosphate, $K_2HPO_4$, 33.4 g disodium hydrogen phosphate heptahydrate, $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g ammonium chloride, $NH_4Cl$, in about 500 mℓ distilled water and dilute to 1 ℓ. The pH of this buffer should be 7.2 without further adjustment. Discard the reagent (or any of the following reagents) if there is any sign of biological growth in the stock bottle.

Magnesium sulfate solution: Dissolve 22.5 g $MgSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 ℓ.

Ferric chloride solution: Dissolve 0.25 g $FeCl_3 \cdot 6H_2O$ in distilled water and dilute to 1 ℓ.

Seeding: The purpose of seeding is to introduce into the sample a biological population capable of oxidizing the organic matter in the wastewater.

When there is reason to believe that the sample contains very few microorganisms, the dilution should be seeded. The standard seed material is settled domestic sewage which has been stored at 20° C for 24-36 hrs. The standard seed concentration is 1-2 mℓ per liter of dilution water." (Standard Methods, 13th Ed., 1971, pp. 489-490).

## Procedures

"Preparation of Dilution Water - Before use, store the distilled water in cotton-plugged bottles long enough to permit it to become saturated with DO; or, if such storage is not practical, saturate the water by shaking the partially filled bottle or by aerating with a supply of clean compressed air. The distilled water should be at 20 ± 1° C.

Place the desired volume of distilled water in a suitable bottle and add 1 mℓ each of phosphate buffer, magnesium sulfate, calcium chloride and ferric chloride solutions for each liter of water. If dilution water is to be stored in the incubator, add the phosphate buffer just prior to using the dilution water.

If the dilution water is seeded, it should be used the same day it is prepared.

Dilution technique: Make several dilutions of the prepared sample so as to obtain the required oxygen depletion. The dilutions to be used should be based on COD or TOC determinations. In leachate from a recently generating fill the BOD concentration can approach 70 percent to 80 percent of the COD value. In such samples, the COD value is generally three times higher than the TOC. in biologically stabilized leachate the BOD may only represent a few percentages of the COD value, as indicated in section 9.1. The dilutions should be chosen such that the oxygen uptake in the diluted sample is less than 7 mg/ℓ.

Carefully siphon standard dilution water into a graduated cylinder of 1,000-2,000 ml capacity, filling the cylinder half full without entrainment of air. Add the quantity of carefully mixed sample to make the desired dilution and dilute to the appropriate level with dilution water. Mix well with a plunger-type mixing rod, avoiding entrainment of air. Siphon the mixed dilution into two BOD bottles, one for incubation and the other for determination of the initial DO in the mixture; stopper tightly and incubate for 5 days at 20° C. The BOD bottles should be water-sealed by inversion in a tray of water in the incubator or by use of a special water-seal bottle. Prepare succeeding dilutions of lower concentration in the same manner or by adding dilution water to the unused portion of the preceding dilution.

The dilution technic may be greatly simplified when suitable amounts of sample are measured directly into bottles of known capacity with a large-tip volumetric pipet and the bottle is filled with sufficient dilution water that the stopper can be inserted without leaving air bubbles. Dilutions greater than 1:100 should be made by diluting the waste in a volumetric flask before it is added to the incubation bottles for final dilution.

Since some of the constituents in leachate such as ferrous iron and sulfide may pose an immediate oxygen demand, the determination of the initial DO should be executed immediately after addition of the diluted sample to the BOD bottle.

Incubation: Incubate the blank dilution water and the diluted samples for 5 days in the dark at 20° C. Then determine the DO in the incubated samples and the blank, using the azide modification of the iodometric method or a membrane electrode. Those dilutions showing a residual DO of at least 1 mg/ℓ and a depletion of at least 2 mg/ℓ should be considered the most reliable.

Seed Correction: Determine the oxygen depletion of the seed by setting up a separate series of seed dilutions and selecting those resulting in 40-70 percent oxygen depletions in 5 days. One of these depletions is then used to calculate the correction due to the small amount of seed in the dilution water. Do not use the seeded blank for seed correction because the 5-day seeded dilution water blank is subject to erratic oxidation due to the very high dilution of seed, which is not characteristic of the seeded sample.

Dilution Water Control: Fill two BOD bottles with unseeded dilution water. Stopper and water-seal one of these for incubation. The other bottle is for determining the DO before incubation. The DO results on these two bottles are used as a rough check on the quality of the unseeded dilution water. The depletion obtained should not be used as a blank correction; it should not be more than 0.2 mℓ and preferably not more than 0.1 mℓ.

Glucose-Glutamic Acid Check: The BOD test is a bioassay procedure; consequently, the results obtained are influenced greatly by the presence of toxic substances or the use of a poor seeding material. Experience has shown that distilled waters are frequently contaminated with toxic substances - most often copper - and that some sewage seeds are relatively inactive. The results obtained with such waters are always low.

The quality of the dilution water, the effectiveness of the seed, and the technic of the analyst should be checked periodically by using pure organic compounds on which the BOD is known or determinable. If a particular organic compound is known to be present such as acetic acid, it may well serve as a control on the seed used. There have been a number of organic compounds proposed, such as glucose or glutamic acid. For general BOD work, a mixture of these (150 mg/ℓ of each) has certain advantages. It must be understood that glucose has an exceptionally high and variable oxidation rate with relatively simple seeds. When used with glutamic acid, the oxidation rate is stabilized.

To check the dilution water, the seed material, and the technic of the analyst, prepare a standard solution containing 150 mg/ℓ each of reagent-grade glucose and glutamic acid which have been dried at 103° C for 1 hr. Pipet 5.0 mℓ of this solution into calibrated incubation bottles, fill with seeded dilution water, and incubate with seed control at 20° C for 5 days. On the basis of a mixed primary standard containing 150 mg/ℓ each of glucose and glutamic acid, the 5-day BOD varies in magnitude according to the type of seed, and precision varies with the quality of seed. "Definition:

$D_1$ = DO of diluted sample directly after preparation
$D_2$ = DO of diluted sample after incubation
P = decimal fraction of sample used
$B_1$ = DO of dilution of seed control before incubation
$B_2$ = DO of dilution of seed control after incubation
f = ratio of seed in sample to seed in control
$= \frac{\%\ \text{seed in } D_1}{\%\ \text{seed in } B_1}$
Seed correction = $(B_1 - B_2)f$

Biochemical oxygen demand: When using seeded dilution water:

$$\text{mg/ BOD} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P} \text{ "}$$

(Standard Methods, 13th Ed., 1971, p. 490-494).

## 9.2 THE COLIFORM DETERMINATION

### Principle

The coliform group comprises all of the aerobic and facultative anaerobic gram negative, non-spore forming, rod shaped bacteria which ferment lactose with gas formation within 48 hr. at 35° C as determined with the multiple tube fermentation technique. When using the rapid and more reproducible membrane filter technique (APHA, 1971) this group is defined as all the aerobic and facultative anaerobic gram negative non-spore forming, rod shaped bacteria which produce a metallic sheen within 24 hours in an endo-type medium containing lactose. The fecal coliform test differentiates between coliforms of fecal origin and originating from warm blooded animals using a confirmatory test incubated at elevated temperatures.

### Interferences

The results of the examination with the multiple tube technique are expressed in terms of a statistical Most Probable Number (MPN) and the estimate generally tends to be greater than the actual numbers (APHA, 1971). An observed limitation of the membrane filter technique is its reduced ability to detect bacteria in turbid samples or in the presence of high concentrations of noncoliform bacteria.

### Previous Studies

Only a limited number of studies (Appendix A) measured this parameter and generally used the multiple tube fermentation technique as opposed to the membrane filter technique.

A comparison by Smith (1972) of the Most Probable Number (MPN) technique with the Membrane Filtration Technique (MF) showed that generally higher readings were obtained with the former method (Figure 37), due to the elaborate enumeration step incorporated in the method. The results of the MPN test are two log cycles higher than the MF test at high coliform concentrations, but are approximately half a log cycle higher at low coliform concentrations. The enumeration step also enables the MPN method to determine low concentrations of bacteria that may not register on the MF test (Smith, 1972). On the other hand the MF method is more precise since it determines actual numbers while the MPN method indicates the expected concentration within certain confidence limits. Glotzbecker (1974) reached a similar conclusion and found that the MPN technique gave results about two log cycles higher than the MF technique at densities of $10^8$-$10^9$ MPN/100 m$\ell$. The two studies did not make a comparison of the MPN and MF methods by analyzing a buffer solution spiked with bacteria in order to determine whether the discrepancy of the two methods is either due to the characteristics of the method itself or of the leachate characteristics.

### Evaluation of Method

To determine whether any of the above results are due to the leachate characteristics, the MF method was tested using both leachate and phosphate buffer to compare the recoveries in each solution. In order to evaluate the effectiveness of the MF procedure, the recovery was tested when bacteria of known concentrations were added to leachate and directly analyzed with the MF technique (Engelbrecht and Amirhor, 1975). The analysis of the leachate sample was conducted immediately after addition of the standard amount to prevent the known logarithmic inactivation of bacteria with time. The leachate was also analyzed before addition of the stock solution to ensure that all bacteria were present at concentrations below their detectable limits. A buffer solution was used as control to which an identical amount of stock solution was added.

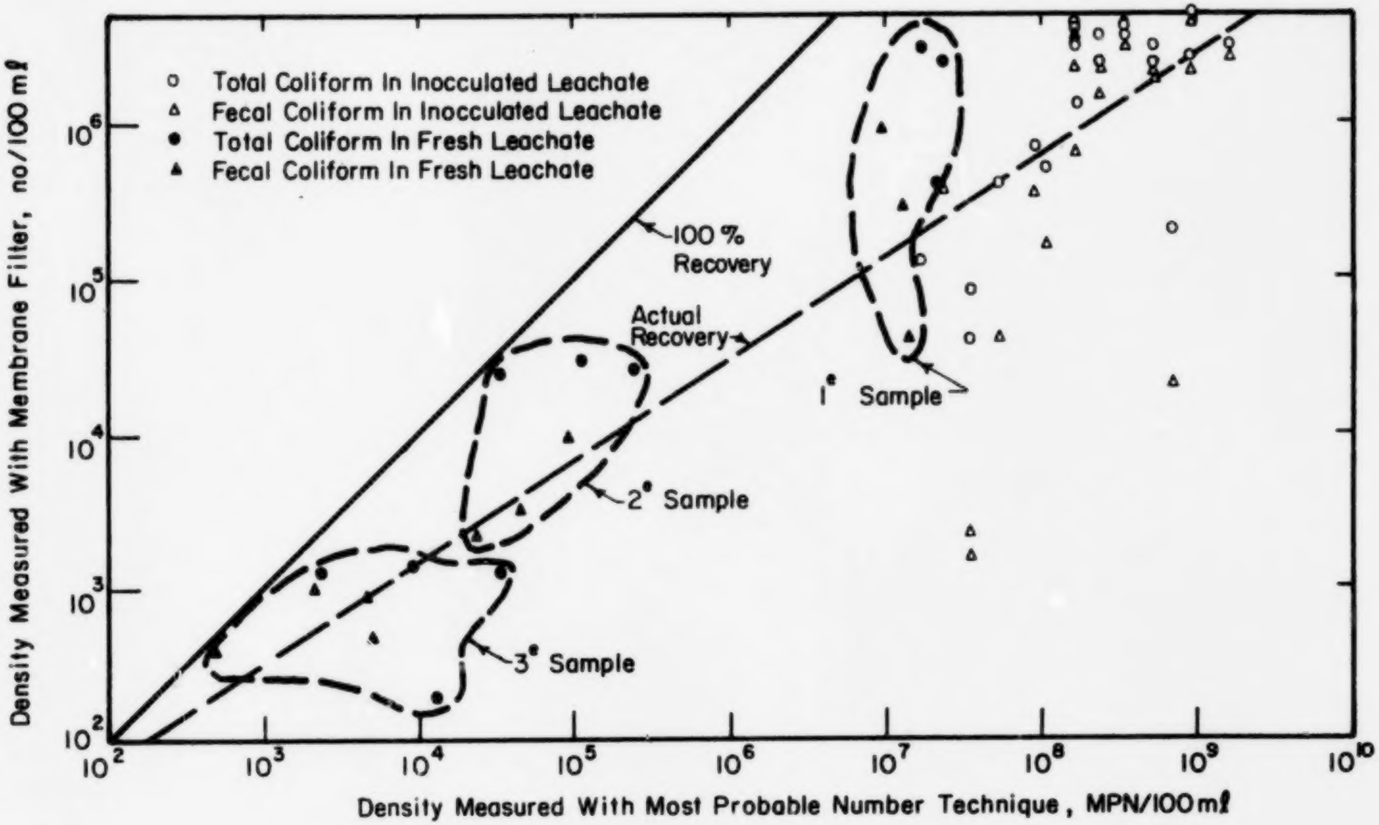

Figure 37. Relation Between Measurement of Total and Fecal Coliforms by Most Probable Number Technique and by Membrane Filtration Technique (Smith, 1972)

The results in Figure 38 (Engelbrecht and Amirhor, 1975) indicate that generally less than 100 percent of salmonella, fecal coliform and fecal streptococci are recovered from the leachate as compared to the buffer solution. The maximum decrease in recovery is approximately half a log cycle. Several samples, however, show a 100 percent or more recovery, indicating that the leachate only causes a relative small decrease in recovery.

The recoveries generally increased when the leachate was centrifuged to remove suspended solids, indicating that the suspended solids slightly interfere in the ability of the MF technique to recover 100 percent of the added bacteria. The recovery also tended to be larger for the high molecular weight organic fraction (retentate of the 500 MW membranes ultrafiltration step) as compared to the low molecular weight fraction (permeate of the 500 MW membrane ultrafiltration step), possibly indicating that the exposure of the bacteria to fatty acids and heavy metals might result in a small instantaneous inactivation. The recoveries also tended to be larger at higher initial bacterial concentrations, indicating that the MF might be more accurate at high bacterial concentrations as opposed to low concentrations. The higher precision of the MF method is illustrated by the relative small scattering of the data in Figure 38, all determined by the MF technique, as compared to the relative larger scattering in Figure 37, using both MF and MPN technique. The above results tentatively indicate that the MF technique results in slightly lower bacterial densities when analyzing leachate as compared to analyzing a buffer solution used as a control. This is possibly due to the presence of suspended solids, which are not expected to similarly affect the MPN technique. The observed immediate inactivation possibly due to fatty acids and heavy metals is expected to cause an identical decrease when using either the MPN or MF technique. It may therefore be concluded that only a part of the two log cycle differences between MPN and MF, to maximum of 25 percent, is due to leachate characteristics such as the presence of suspended solids, while the main difference is due to the different nature of the two tests, i.e. the inclusion of an enumeration step in the MPN method.

## Recommendations

The MPN technique should be selected for leachate monitoring purposes as opposed to the MF technique, since it is able to detect bacteria at lower concentrations and is less subject to suspended solids interference. Inactivation studies, however, in which a certain amount of bacteria is added to a sample to study its subsequent reduction with time, should be conducted with the MF technique.

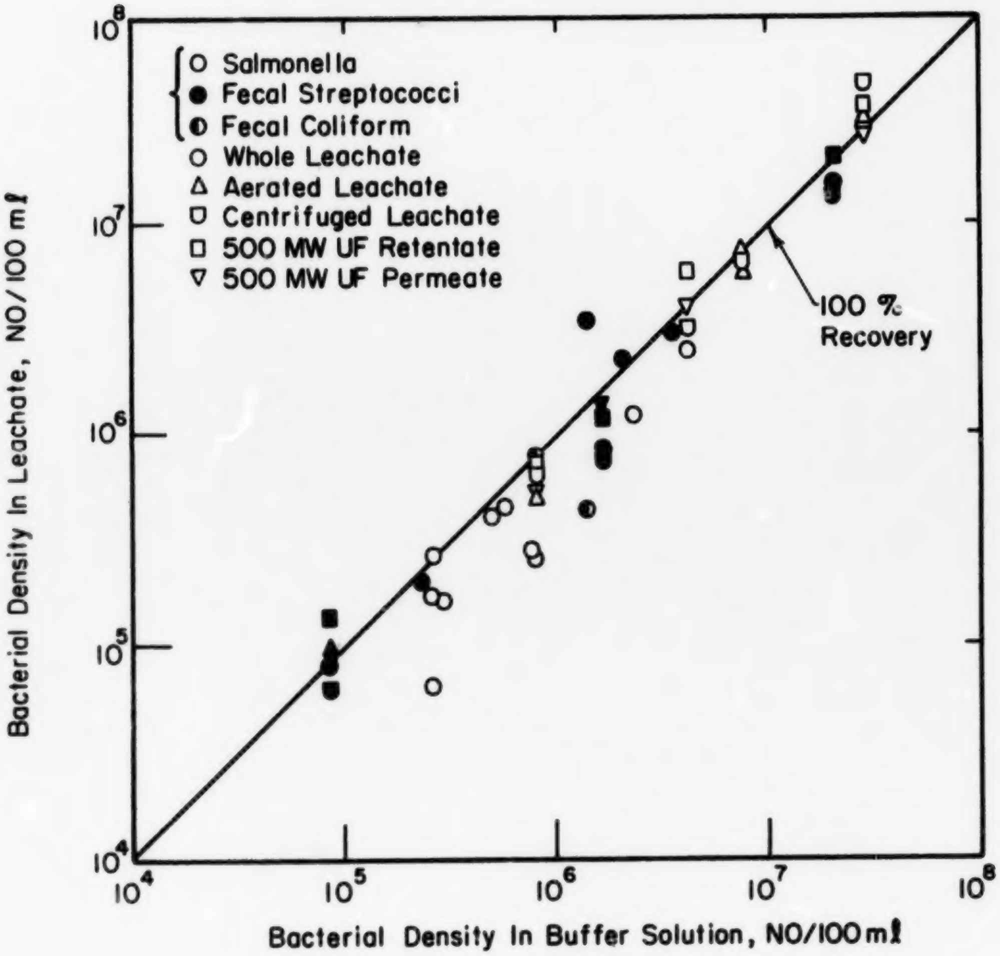

Figure 38. Recovery of Bacteria Added in Identical Amounts to a Buffer Solution and a Leachate Sample Respectively, Both Maintained at 25° C Immediately After Its Addition (Engelbrecht and Amirhor, 1975)

## Reagents

Most studies evaluated generally use lauryl tryptose broth and sometimes lactose broth for the presumative total coliform test in leachate (Blannon and Peterson, 1973; Appendix A). When 1 ml or less of sample is added to 10 ml of medium, 35.6 g/l dehydrated lauryl tryptose broth is measured. When 10 ml inocculum is added to 10 ml of medium double the amount is measured (APHA, 1971).

Most studies use brilliant green lactose bile broth and sometimes endo agar plates for the confirmatory test in leachate (Blannon and Peterson, 1973; Appendix A). The medium consists of 10 g peptose, 10 g lactose, 10 g oxgall, 13.3 mg brilliant green in 1 ℓ of distilled water (APHA, 1971).

Most studies that test for fecal coliforms use EC medium (Blannon and Peterson, 1973; Appendix A) consisting of .20 g Tryptose, 5 g lactose, 1.5 g bile salts, 4 g dipotassium hydrogen phosphate, 1.5 g potassium dihydrogen phosphate and 5 g sodium chloride in 1 ℓ distilled water.

## Procedures of Presumptive Test for Total Coliforms

"Inoculate a series of fermentation tubes, 'primary' fermentation tubes, with appropriate graduated quantities, of the water to be tested. The portions of the water sample used for inoculating the lauryl tryptose broth fermentation tubes will vary in size and number with the character of the water under examination, but should be decimal multiples and submultiples of 1 ml. These should be selected in accordance with the discussion of the multiple-tube test above.

Incubate the inoculated fermentation tubes at 35 ± 0.5°C. After shaking gently, examine each tube at the end of 24 ± 2 hrs and, if no gas has formed and been trapped in the inverted vial, again at the end of 48 ± 3 hr. Record the presence or absence of gas formation at each examination of the tubes, regardless of the amount.

Formation within 48 ± 3 hr of gas in any amount in the inner fermentation tubes or vials constitutes a positive Presumptive Test." (Standard Methods, 13th Ed., 1971, pp. 664-665).

## Procedures of Confirmed Test for Total Coliforms

"Submit all primary fermentation tubes showing any amount of gas at the end of 24 hr of incubation to the confirmed test. If active fermentation appears in the primary fermentation tube before expiration of the 24 hr period of incubation, it is preferable to transfer to the confirmatory medium without waiting for the full 24-hr period to elapse. If additional primary fermentation tubes show gas production at the end of 48-hr incubation, these too shall be submitted to the confirmed test.

Gently shake or rotate primary fermentation tube showing gas and with a sterile metal loop, 3 mm in diameter, transfer one to three loopfuls of medium to a fermentation tube containing brilliant green lactose bile broth

Incubation - Incubate the inoculated brilliant green lactose bile broth tube for 48 ± 3 hrs at 35 ± 0.5° C.

Interpretation - The formation of gas in any amount in the inverted vial of the brilliant green lactose bile broth fermentation tube at any time within 48 ± 3 hr constitutes a positive Confirmed Test." (Standard Methods, 13th Ed., 1971, pp. 665-666). The calculation of the Most probable Number should proceed according to Standard Methods (APHA, 1971) using probability tables. The complete coliform test should be conducted in those instances where leachate causes pollution of drinking water supplies.

## Procedures for the Fecal Coliform Test

"Transfers should be made from all positive presumptive tubes to EC medium. This examination may be performed simultaneously with the confirmatory procedure using brilliant green lactose bile broth. Use a sterile metal loop with a minimum 3 mm diameter to transfer from the positive fermentation tube to EC medium. When making such transfers, first gently shake the presumptive tube or mix by rotating. Inoculated tubes are incubated in a water bath at 44.5 ± 0.2° C for 24 ± 2 hrs. All EC tubes must be placed in the water bath within 30 min after plating. The water depth in the incubator should be sufficient to immerse tubes to the upper level of the medium.

Interpretation - Gas production in a fermentation tube within 24 hr or less is considered a positive reaction indicating fecal origin. Failure to produce gas (growth sometimes occurs) constitutes a negative reaction indicating a source other than the intestinal tract of warm-blooded animals." (Standard Methods, 13th Ed., 1971, p. 669). Fecal coliform densities are calculated as Most Probable Number using probability tables in Standard Methods (APHA, 1971).

# SECTION 10

# MISCELLANEOUS DETERMINATIONS

Only very few studies measured parameters not discussed earlier. Only two studies measured LAS while another study measured MBAS. Two studies measured CN while one study measured F. Three studies measured the DO but this parameter is less useful than the ORP and is therefore not recommended. Two studies measured sulfides, while one study measured $SiO_2$. One study measured hexane solubles while another measured ether solubles, however, the weight of both extractions is enhanced by the presence of free volatile fatty acids (Appendix A).

The color parameter has been determined in some of the studies and may have potential as an indicator parameter to signal high organic matter concentration. Since turbidity is sometimes difficult to remove from leachate samples, the method will only record apparent color. Because of its inaccuracy the platinum cobalt method is not recommended. The EPA (1974) recommends the spectrophotometric method by measuring transmittance at several wavelengths. Technicon (1973) recommends absorbance readings at 400 nm and using platinum cobalt as standard curve.

Several studies report the visual appearance and odor of the leachate sample before analysis and such evaluation is useful since it gives a general characterization while it is not time consuming.

# SECTION 11

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# SECTION 12

# APPENDIX A

Survey of physical, chemical, and biological methods used by various investigators.

Apgar and Langmuir (1971)

| Parameter | Method |
|---|---|
| pH | Combination glass electrode, Sargent Welch PBX |
| Oxidation/Red. Potent. | Pt and Kalomel electrode; Beckman Model G |
| Conductivity | Beckman cond. meter Model RC-1982, cell constant $1.\text{cm}^{-1}$ |
| Total Solids, Volatile | N/A* |
| Suspended Solids, Volatile | N/A |
| Chemical Oxygen Demand | N/A |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | N/A |
| Chlorides | $AgNO_3$ titration |
| Sulfates | Turbidimetric method |
| Phosphate | $SnCl_2$ Method |
| Alkalinity/Acidity | Titration to pH 4.5 |
| Nitrate | Specific ion electrode; phenol disulfonic acid |
| Nitrite | Sulfanilic method |
| Ammonia-N | Nessler method |
| Na, K | Flame photometer |
| Ca, Mg | Atomic absorption |
| Hardness | N/A |
| Heavy Metals | Fe, metals with atomic absorption on acidified samples |
| Biochemical Oxygen Demand | DO measured in diluted leachate |
| Coliform | N/A |
| Standard Plate Count | N/A |
| Gasses | N/A |
| Miscellaneous | Temperature DO color (qual.); odor (qual.); turbidity (qual.) |

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*N/A parameter was not analyzed for

Black and Veatch/Charleston Labs

| Parameter | Method |
|---|---|
| pH | Glass electrodes |
| Oxidation-Reduction Pot. | N/A |
| Conductivity | N/A |
| Total Solids, Volatile | Constant weight at 105° C |
| Suspended Solids, Volatile | N/A |
| Chemical Oxygen Demand | Dichromate |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | Kjeldahl digestion and distillation |
| Chlorides | Argentometric method with $AgNO_3$ |
| Sulfates | $BaSO_4$ turbidimetric |
| Phosphates | $SnCl_2$ method for ortho-P |
| Alkalinity, Acidity | Methyl orange endpoint |
| Nitrates | N/A |
| Nitrites | N/A |
| Ammonia-N | Kjeldahl distillation |
| Na, K | Flame photometry |
| Ca | Ca with permanganate titrimetric method |
| Mg | Mg with gravimetric method using diammonium hydrogen phosphate |
| Hardness | EDTA titration |
| Heavy Metals | Mn with persulfate method; Zn with dithizon method; Cd with dithizone method; Pb with dithizone method; B with carmine method; Cr with diphenyl carbazide method; As with diethyldithiocarbamate method |
| Biochemical Oxygen Demand | N/A |
| Coliforms | N/A |
| Total Plate Count | N/A |
| Gasses | N/A |

| Parameter | Cameron and McDonald (1974) Method |
|---|---|
| pH | Glass electrode, SCE- |
| ORP | N/A |
| Conductivity | N/A |
| Total Solids Volatile | 105° C overnite, 550° C for 1 hr |
| Suspended Solids Volatile | Glass fiber filter |
| Chemical Oxygen Demand | Dichromate |
| Total Organic Carbon | Beckman TOC analyzer, inorganic channels fouled by leachate |
| Volatile Acids | N/A |
| Tannins, Lignins | Folin-Dennis test, color reading after 10 minutes |
| Organic-N | Kjeldahl, distillation |
| Chlorides | Specific ion electrode with 1:1 sample diluted 1 M $KNO_3$ |
| Sulfates | $BaCl_2$ added to precip $SO_4$, excess Ba with AA or turbidimetric |
| Phosphate | $SnCl_2$, persulfate digestion for 30 min at 15 psi |
| Alkalinity/Acidity | Titrated to pH 3.7 and 8.3 |
| Nitrate | Cu, Cd reduction with autoanalyzer, determined immediately after collection |
| Nitrite | Cu/Cd reduction |
| Ammonia N | Distillation, titration or specific ion electrode at pH 11 |
| Na, K | Atomic absorption spectroscopy |
| Ca, Mg | Atomic absorption spectroscopy |
| Hardness | From individ. ions |
| Heavy Metals | Jarrel Ash MV-500 AA; background correction at nonabsorbing bordering line Pb, Cr, Ti, Mo, V concentrated with $BiNO_3$ coprecipitation at pH 5.5 after acid digestion; No modification for Cd, Cu, Ni, Be and Ba; 4:1 conc $HCl/HNO_3$ acid digestion at 5% of sample volume; Hg with flameless AA immed. after collection; Ba with AA and 2000 mg/l K. As with diethyldithiocarbamate method immed. after collection, B with curcumin after filtration of alcohol solution, Se with AA as hydrogen selenide. |
| Biochemical Oxygen Demand | DO probe or Azide modification; no seeding; $BOD_5$ is 75% of $BOD_2$. |
| Coliform | MPN immed. after collection |

Cameron and McDonald (1974)

| Parameter | Method |
|---|---|
| Standard Plate Count | N/A |
| Gasses | Fisher gas partitioner for $CO_2$, $N_2$, $O_2$, $CH_4$ and $H_2S$ 200 ma filament current; helium flow 30 ml/min; 12 feet 15% Ucon 50-HB 280 on 40/60 mesh teflon Pb, 5 feet Chromasorb P, 7 feet molecular sieve 13X |
| Miscellaneous | CN determ. immed. after collect, with distillation; Color with Hellige Aquatester; F with specific ion electrode after ionic strength adjustment with 10 g/l cyclohexylene dimitrilotetraacetate acid (CDTA); $S^=$ with distillation and titration |

Chian and DeWalle (1973)

| Parameter | Method |
|---|---|
| pH | Glass electrode, Beckman Zeromatic SS-3 pH meter |
| Oxidation/Red. Potent. | Pt and Kalomel electrode |
| Conductivity | Yellow Springs |
| Total Solids, Volatile | Drying to constant weight at 105° C, 1 hr at 550° C |
| Suspended Solids, Volatile | Glass fiber filter, GFC Whatman, constant weight at 105° C, 1 hr at 550° C |
| Chemical Oxygen Demand | Dichromate reflux |
| Total Organic Carbon | Beckman TOC analyzer IR-215-B acidified sample |
| Volatile Acids | Hewlett-Packard Research Chromatograph 5750 |
| Tannins, Lignins | Molybdophosphoric acid |
| Organic-N | Kjeldahl, titration |
| Chlorides | Potentiometer titration |
| Sulfates | $BaSO_4$ precipitation method |
| Phosphate | Persulfate digestion and ascorbic acid method |
| Alkalinity/Acidity | Titration to inflection point of titration curve |
| Nitrate | Brucine method electrode |
| Nitrite | Sulfanilic acid |
| Ammonia-N | Kjeldahl, titration |
| Na, K | Flame photometer, Cs added |
| Ca, Mg | Atomic absorption, La added |
| Hardness | Calculated from concentrations |
| Heavy Metals | Atomic Absorption with standard addition |
| Biochemical Oxygen Demand | Seeding/No seeding, Precision Scientific Galvanic Cell DO meter |
| Coliform | Kjeldahl, titration, membrane filter |
| Standard Plate Count | Bacto plate count agar |
| Gasses | Fisher Hamilton gas partitioner |
| Miscellaneous | Color absorbance at 400 nm; turbidity |

**EPA-SHWRL NERC-Cincinnati; Bramble (1971)**

| Parameter | Method |
|---|---|
| pH | Combination glaselectrode |
| Oxidation/Red. Poten. | N/A |
| Conductivity | Cond. bridge |
| Total Solids, Volatile | 1 hour at 105°C, 30 min at 600°C |
| Suspended Solids, Volatile | Glass fiber filter in gooch crucible |
| Chemical Oxygen Demand | Dichromate reflux 50 ml sample, 1 g $HgSO_4$, 1 g $Ag_2SO_4$, 25 ml 0.25 N $K_2Cr_2O_7$, 70 ml $H_2SO_4$ |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | Kjeldahl, titration |
| Chlorides | $HgNO_3$ titration |
| Sulfates | Turbidimetric with Hach sulfaver reagent, on filtered samples |
| Phosphate | Aminonaphtol sulfonic acid |
| Alkalinity | Phenolphthalein, methyl orange endpoint |
| Nitrate | Brucine method; Cd reduction method |
| Nitrite | Cd reduction method |
| Ammonia-N | Kjeldahl titration |
| Na, K | Flame photometer |
| Ca, Mg | Atomic absorption, Varian Techtron |
| Hardness | EDTA titration, CN added; sometimes fading endpoint; filtration no effect |
| Heavy Metals | Perkin Elmer Atomic 303 Absorption, Mn, Fe, Zn |
| Biochemical Oxygen Demand | No seeding; Weston and Stack DO memter and azide modification of Winkler test; BOD blacktop layer 2340 mg/l; middle 3015; mixed 3320. Winkler/Azide is 10.1% higher than DO meter |
| Coliform | Most probable number |
| Total Plate Count | N/A |
| Gasses | Fisher gas partitioner |
| Miscellaneous | Ether extractables |

**Fungaroli (1971)**

| Parameter | Method |
|---|---|
| pH | Glass electrode; 10% $KNO_3$ Orion reference electrode instead of calomel |
| Oxidation/Red. Poten. | N/A |
| Conductivity | N/A |
| Total Solids, Volatile | Air drying followed by drying to constant weight at 102°C, 10 min at 600°C |
| Suspended Solids, Volatile | Glass fiber filter on Pyrex glass filter holder; GFC-Whatman glass paper, 1 hr at 103°C, 10 min at 600°C |
| Chemical Oxygen Demand | 20 mℓ sample, 15 mℓ $H_2SO4$ with $Ag_2SO_4$, 5 mℓ 0.5 N $K_2Cr_2O_7$ 0.11 g $H_gSO_4$ titration with 0.10 N FAS |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | $HgCl_2$ tablet and 10 mℓ conc. $H_2SO_4$ replaces the acid catalyst; digestion for 90 min. |
| Chlorides | Orion combined reference - chloride ion electrode with Beckman expandometric potentiometer |
| Sulfates | Turbidimetric method measured with Bausch Lamb Spectronic 20 |
| Phosphate | Aminonaphtol sulfonic acid method when high conc. of organic matter are present; otherwise $SnCl_2$ method |
| Alkalinity | Titration with 0.02 N $H_2SO_4$ to pH 4.5 |
| Nitrate | UV absorption at 220 $m\mu$ after acidification, organic matter interference corrected by measuring at 275 $m\mu$ |
| Nitrite | N/A |
| Ammonia-N | Kjaldahl, distillate collected in boric acid, titrated to pH 4.5 |
| Na, K | Flame photometer, Coleman No. 21 |
| Ca, Mg | Ca with EDTA titration after $Mg(OH)_2$ is precipitated by pH adjustment; flame photometer |
| Hardness | EDTA titration, NaCN buffer |
| Heavy Metals | Beckman atomic absorption, 3 mℓ 1:1 $HNO_3$ added for presentation centrifuged to remove turbidity Fe, Zn, Ni, Cu |
| Biochemical Oxygen Demand | DO measured with Delta Sc DO meter and Winkler azide modification test; no seeding; elimination of immediate oxygen demand by preaeration or measuring DO in BOD bottle after 15 min. |
| Coliform | N/A |
| Total Plate Count | N/A |
| Gasses | Fisher Hamilton gas partitioner $CO_2$, $O_2$, $N_2$, $H_2S$, $CH_4$ |
| Miscellaneous | DO |

Golueke (1974)

| Parameter | Method |
|---|---|
| pH | Combination electrode radiometer model 22 pH meter |
| Oxidation-Reduction Pot. | N/A |
| Conductivity | YSI Model 31 |
| Total Solids,Volatile | Dry at 105° C,muffle 1 hr at 580° C |
| Suspended Solids, Volatile | GFC filter dry at 105° C, 1 hr at 580° C |
| Chemical Oxygen Demand | Dichromate reflux |
| Total Organic Carbon | Beckman TOC analyzer, IR 215 |
| Volatile Acids | Total;column partition chromatography |
| Tannins, Lignins | N/A |
| Organic-N | Kjeldahl |
| Chlorides | $Hg(NO_3)_2$ titration |
| Sulfates | $Ba_2SO_4$ precipitation |
| Phosphates | Ammonium molybdate - strong acid digestion |
| Alkalinity, Acidity | Titration to pH 4.3 |
| Nitrates | Brucine |
| Nitrites | N/A |
| Ammonia-N | Kjeldahl |
| Na, K | Flame protometer, Beckman DV |
| Ca | EDTA titration |
| Mg | EDTA titration |
| Hardness | EDTA titration |
| Heavy Metals | Atomic absorption |
| Biochemical Oxygen Demand | Seeded |
| Coliforms | N/A |
| Total Plate Count | Standard Plate Count |
| Gasses | Varion Gas Chromatograph TC Detector |

Ho, Boyle and Ham (1971) Boyle and Ham (1972)

| Parameter | Method |
|---|---|
| pH | Orion Research, Inc. Ionalizer Model 404 |
| Oxidation/Red. Poten. | N/A |
| Conductivity | Labline Electro MHO meter MC-1; Cell constant 1.0 |
| Total Solids, Volatile | N/A |
| Suspended Solids Volatile | N/A |
| Chemical Oxygen Demand | N/A |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | Kjeldahl digestion with digestion reagent sulfuric acid $K_2SO_4$ $HgSO_4$; titration |
| Chlorides | $HgNO_3$ method |
| Sulfates | N/A |
| Phosphate | Persulfate digestion $SnCl_2$,organic separation extraction |
| Alkalinity | Titration to pH 4.3 |
| Nitrates | *Keeney digestion with devarde alloy,125 ml erlenmeyer,P buffer, boric acid |
| Nitrite | Keeney digestion; MgO added; only $NH_4$, excluding $NO_2$, $NO_3$ |
| Ammonia-N | Same as above |
| Na, K | N/A |
| Ca, Mg | Ca Hardness, Calver-2 No. 281added (Hach) |
| Hardness | CN added; EDTA titration; for total hardness Univer I No. 206 added (Hach) |
| Heavy Metals | Fe phenanthroline method |
| Biochemical Oxygen Demand | N/A |
| Coliform | N/A |
| Total Plate Count | N/A |
| Gasses | N/A |

*Brenner, J. M. and Keeney D. R., "Steam Distillation Method for Determination of Ammonia, Nitrates and Nitrites," Anal. Chem. Acta, 32, 485-495 (1965).

Holzer and Chestnut (1974)

| Parameter | Method |
|---|---|
| pH | Beckman Instruments, expandomatic pH meter |
| Oxidation-Reduction Pot. | N/A |
| Conductivity | Beckman Instruments RB3, Solu Bridge |
| Total Solids, Volatile | N/A |
| Suspended Solids, Volatile | N/A |
| Chemical Oxygen Demand | N/A |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | N/A |
| Chlorides | Mercurimetric method |
| Sulfates | Thorin Method |
| Phosphates | Only Ortho-P, Phosphomolybate method |
| Alkalinity, Acidity | Titration to pH = 4.5 |
| Nitrates | Brucine method |
| Nitrites | N/A |
| Ammonia-N | N/A |
| Na, K | Atomic adsorption |
| Ca | Atomic adsorption |
| Mg | Atomic adsorption |
| Hardness | N/A |
| Heavy Metals | Atomic absorption;sample acidified |
| Biochemical Oxygen Demand | N/A |
| Coliforms | N/A |
| Total Plate Count | N/A |
| Gasses | N/A |

Hughes et al. (1971)

| Parameter | Method |
|---|---|
| pH | Glass electrode, Beckman pH meter |
| Oxidation/Red. Potent. | N/A |
| Conductivity | Measured as TDS (NaCl equiv.) |
| Total Solids, Volatile | Dried at 105° C |
| Suspended Solids, Volatile | N/A |
| Chemical Oxygen Demand | Dichromate reflux, $Ag_2SO_4$ added to precipitate Cl |
| Total Organic Carbon | N/A |
| Volatile Acids | Hydroxylamine test |
| Tannins, Lignins | N/A |
| Organic-N | Total Kjeldahl |
| Chlorides | $Hg(NO_3)_2$ and argentometric method after filtration |
| Sulfates | Turbidimetric after filtration |
| Phosphate | Ascorbic acid |
| Alkalinity/Acidity | Methylorange titration; potentiometric titration to pH 4.5 |
| Nitrate | Phenol disulfonic method after filtration |
| Nitrite | Measured with $NO_3$ |
| Ammonia-N | Total Kjeldahl |
| Na, K | Na estimated from dissolved fixed residue and hardness |
| Ca, Mg | EDTA titration |
| Hardness | EDTA titration |
| Heavy Metals | Fe with phenanthroline method and tripyridine method, Mn with persulfate method |
| Biochemical Oxygen Demand | 20 d. test seeded with sewage |
| Coliform | N/A |
| Standard Plate Count | N/A |
| Heavy Metals | Cu, Cd, Pb, Zn, Fe, Cr, Se, Al, As, Be with Jarrel-Ash Atom. Absorp. Spect. 30 min. digest with 1 percent dil. nitric acid; internal standards for As,B with carmine method |
| Miscellaneous | CN,F MBAS foaming interface hexane sol. fluorescence |

### A. W. Martin (1974)

| Parameter | Method |
|---|---|
| pH | Leeds Northrop pH meter |
| Oxidation/Red. Potent. | N/A |
| Conductivity | N/A |
| Total Solids, Volatile | 103° C for 60 minutes (two weighings), 550° C for 30 minutes (two weighings) |
| Suspended Solids Volatile | N/A |
| Chemical Oxygen Demand | Dichromatic; more $HgSO_4$ added |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | Kjeldahl and Nessler |
| Chlorides | $AgNO_3$; dichromate endpoint |
| Sulfates | $BaSO_4$ turbidimetric |
| Phosphate | Persulfate digestion; vanadomolybdate |
| Alkalinity/Acidity | Methylorgange and phenolphtalen endpoint |
| Nitrate | Brucine |
| Nitrite | Sulfanilic acid |
| Ammonia-N | Kjeldahl and Nessler |
| Na, K | AA |
| Ca, Mg | AA |
| Hardness | AA |
| Heavy Metals | Fe colorimetric, Fe, Pb, Cu, Zn, Ni, Hg, Cr, with AA |
| Biochemical Oxygen Demand | Seed from polluted creek; Yellow Spring DO meter |
| Coliform | N/A |
| Standard Plate Count | N/A |
| Gasses | N/A |
| Miscellaneous | N/A |

Merz (1954)

| Parameter | Method |
|---|---|
| pH | Glass electrode, Beckman portable |
| Oxidation/Red. Potent. | N/A |
| Conductivity | N/A |
| Total Solids, Volatile | N/A |
| Suspended Solids, Volatile | N/A |
| Chemical Oxygen Demand | N/A |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | Kjeldahl |
| Chlorides | Mohr's test |
| Sulfates | turbidimetric method, $BaSO_4$ precipitation method |
| Phosphate | $SnCl_2$ ammonium molybdate method |
| Alkalinity/Acidity | Volumetric method |
| Nitrate | Measured |
| Nitrite | N/A |
| Ammonia-N | Kjeldahl |
| Na, K | Flame photometer |
| Ca, Mg | Mg with Titan-yellow method |
| Hardness | Sodium versenate method |
| Heavy Metals | Fe with dipyridyl method |
| Biochemical Oxygen Demand | Seeded with settled sewage |
| Coliform | N/A |
| Standard Plate Count | N/A |
| Gasses | N/A |
| Miscellaneous | DO |

### Otton and McKenzie, Geological Survey, Portland (1974)

| Parameter | Method |
|---|---|
| pH | Sargent Welch model PBL glass combination electrode |
| Oxidation-Reduction Pot. | |
| Conductivity | Beckman |
| Total Solids, Volatile | N/A |
| Suspended Solids, Volatile | N/A |
| Chemical Oxygen Demand | N/A |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | N/A |
| Chlorides | N/A |
| Sulfates | N/A |
| Phosphates | N/A |
| Alkalinity, Acidity | N/A |
| Nitrates | N/A |
| Nitrites | N/A |
| Ammonia-N | N/A |
| Na, K | N/A |
| Ca, Mg | N/A |
| Hardness | N/A |
| Heavy Metals | N/A |
| Biochemical Oxygen Demand | N/A |
| Coliforms | Millipore filter;difco media |
| Total Plate Count | N/A |
| Gasses | N/A |

Pedco Environmental (1974)

| Parameter | Method |
|---|---|
| pH | Glass electrode |
| Oxidation/Red. Poten. | N/A |
| Conductivity | Conductivity meter |
| Total Solids, Volatile | Evaporate;1 hour at 105°C |
| Suspended Solids, Volatile | 0.45 μ membrane filter |
| Chemical Oxygen Demand | Dichromate reflux |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | $H_2SO_4$ digestion with HgO + $K_2SO_4$, distillation and titration |
| Chlorides | $HgNO_3$ |
| Sulfates | Turbidimetric |
| Phosphate | Aminonaphtol sulfonic acid |
| Alkalinity | Titration to pH 4.2 and 8.3 |
| Nitrate | Remove Cl, evaporate sample, add PDSA, heat 15 min 90°C, add water and $NH_4OH$, read at 410 nm |
| Nitrite | Sulfanilamide |
| Ammonia-N | Distillation and Titration |
| Na. K | AA |
| Ca, Mg | AA, La added |
| Hardness | EDTA titration |
| Heavy Metals | Nitric acid digestion followed by AA |
| Biochemical Oxygen Demand | Seeded |
| Coliform | N/A |
| Total Plate Count | N/A |
| Gasses | Chromasorb 102, molecular sieve |
| Miscellaneous | |

Department of Environmental Resources, Pennsylvania

| Parameter | Method |
|---|---|
| pH | LTN, Beckman glass electrode |
| Oxidation-Reduction Pot. | N/A |
| Conductivity | Aquatronic model 320 |
| Total Solids, Volatile | Constant weight at 105° C, 1 hr at 550° C |
| Suspended Solids, Volatile | Glass fiber filter GFC Whatman |
| Chemical Oxygen Demand | Dichromate reflux |
| Total Organic Carbon | Beckman TOC analyzer model 915 |
| Volatile Acids | N/A |
| Tannins, Lignins | V. V. Full Scan |
| Organic-N | Automated-EPA digestion + phenolate including $NH_4$ |
| Chlorides | Automated-EPA ferricyanide |
| Sulfates | Automated-EPA Bachla |
| Phosphates | Automated-EPA ascorbic acid |
| Alkalinity, Acidity | Titration to inflection point |
| Nitrates | Automated-EPA Cd reduction (includes nitrite) |
| Nitrites | Automated-EPA diazatization includes $NO_3$ |
| Ammonia-N | Automated-EPA phenolate method |
| Na, K | Flame photometry Cs added |
| Ca, Mg | Atomic absorption La added |
| Hardness | Automated-EPA Calmagite |
| Heavy Metals | Atomic Absorption |
| Biochemical Oxygen Demand | Seeded |
| Coliforms | |
| Total Plate Count | Millipore membrane |
| Gasses | |

| | Qasim (1965); Lin (1966) |
|---|---|
| Parameter | Method |
| pH | Beckman Expendomatic |
| Oxidation/Red. Poten. | N/A |
| Conductivity | N/A |
| Total Solids, Volatile | Drying for 1 hour at 103°C; 15 min at 600°C |
| Suspended Solids, Volatile | N/A |
| Chemical Oxygen Demand | N/A |
| Total Organic Carbon | N/A |
| Volatile Acids | Stream distillation; Gas Chromatograph; Barber Coleman 5000; Selecta with H flame detector, recorder and integrator, recorder and integrator; 16% carbowax 20 M + 2% $H_3PO_4$ on 60/80 mesh |
| Tannins, Lignins | Tyrosine-Hach method |
| Organic-N | Kjeldahl digestion |
| Chlorides | $HgNO_3$ titration |
| Sulfates | Turbidimetric with Hach sulfate reagent |
| Phosphate | $SnCl_2$ |
| Alkalinity | Titration to endpoint determined from titration curve 3.8 and 7.2 |
| Nitrate | Brucine method; aluminum reduction with distillation |
| Nitrite | Sulfanilic acid |
| Ammonia-N | Kjeldahl distillation |
| Na, K | Beckman DU flame photometer |
| Ca, Mg | Ca with EDTA titration (murexide) Mg with brilliant yellow dye or calculated for total hardness and Ca-bacteria |
| Hardness | EDTA titration chrome Black T |
| Heavy Metals | Hach method, Fe with phenanthroline method; phenanthroline method Al with aluminon, B with Carmine, Cu with Cuprethol, Mn with perjodate |
| Biochemical Oxygen Demand | No seeding, DO measured with azide modification |
| Coliform | Presumptive test with lactose broth, 35°C for 48 hour; multiple tube dilution |
| Total Plate Count | Trypton glucose yeast agar at 20°C for 48 hour |
| Gasses | Beckman GC-2A gas chromatograph with molecular sieve 13x and silica gel column |
| Misc. | ABS with methyl green test; $SiO_2$ with amino acid method; $H_2S$ with iodine thiosulfate |

## Rovers and Farquhar (1972)

| Parameter | Method |
|---|---|
| pH | Glass electrode, anal. immediately |
| Oxidation/Red. Potent. | N/A |
| Conductivity | N/A |
| Total Solids, Volatile | Dried to constant weight at 103° C, volatile residues for 30 min at [illegible] |
| Suspended Solids, Volatile | Gooch crucib[illegible] asbestos fiber, dried to constant weight at 1C[illegible] |
| Chemical Oxygen Demand | reflux time up to 7 hr. recommended |
| Total Organic Carbon | |
| Volatile Acids | |
| Tannins, Lignins | |
| Organic-N | Technicon Autoanalyzer; digestion with sulfuric acid and potassium persulfate |
| Chlorides | Titration |
| Sulfates | Turbidimetric. gravimetric |
| Phosphate | Technicon Autoanalyzer total, soluble measured |
| Alkalinity/Acidity | Titration with $H_2SO_4$ to pH 4.5 titration with NaOH to 8.3 no inflection point observed |
| Nitrate | Measured |
| Nitrite | Measured |
| Ammonia-N | |
| Na, K | Flame photometry |
| Ca, Mg | |
| Hardness | EDTA titration; Fe included |
| Heavy Metals | Fe colorimetric; Mn, Cr, Ni, Cd, Cu, Zn by AAS |
| Biochemical Oxygen Demand | Acclimated seed recommended |
| Coliform | |
| Standard Plate Count | |
| Gasses | Model 25V Fisher Gas Partitioner; Perkin Elmer Coleman Recorder, $H_2S$ by Drager Multi Gas Detector Model 21/31 |
| Miscellaneous | |

Sangrey and Bisogni (1974)

| Parameter | Method |
|---|---|
| pH | Glass electrode Beckman Zeromatic SS-3 pH meter |
| Oxidation-Reduction Pot. | N/A |
| Conductivity | N/A |
| Total Solids, Volatile | Drying to constant weight at 105° C, 1 hr at 550° C |
| Suspended Solids, Volatile | Glass fiber filter, GFC Whatman, constant weight at 105° C, 1 hr at 550° C |
| Chemical Oxygen Demand | Dichromate reflux method |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | Kjeldahl, Nesslerization |
| Chlorides | Titration with Mercuric nitrate |
| Sulfates | $BaSO_4$ precipitation |
| Phosphates | Amino-reduction molybdenum blue |
| Alkalinity, Acidity | Titration to inflection point of titration curve |
| Nitrates | N/A |
| Nitrites | N/A |
| Ammonia N | Kjeldahl, Nesslerization |
| Na, K | N/A |
| Ca | N/A |
| Mg | N/A |
| Hardness | N/A |
| Heavy Metals | N/A |
| Biochemical Oxygen Demand | N/A |
| Coliforms | N/A |
| Total Plate Count | N/A |
| Gasses | N/A |

SCS Engineers (1974)

| Parameter | Method |
|---|---|
| pH | Glass and calomel electrode |
| Oxidation/Red. Potent. | |
| Conductivity | Specific conductance |
| Total Solids, Volatile | 105° C |
| Suspended Solids, Volatile | TFC glass fiber filtration |
| Chemical Oxygen Demand | Dichromate reflux |
| Total Organic Carbon | |
| Volatile Acids | |
| Tannins, Lignins | |
| Organic-N | Total Kjeldahl, digestion, distillation and titration |
| Chlorides | $HgNO_3$ |
| Sulfates | Gravimetric |
| Phosphate | $SnCl_2$ |
| Alkalinity/Acidity | |
| Nitrate | Brucine |
| Nitrite | |
| Ammonia-N | Distillation and titration |
| Na, K | |
| Ca, Mg | |
| Hardness | EDTA titration |
| Heavy Metals | Clear samples acidified, 10 x concentr. pollut. samples nitric/sulfuric acid digestion, 5 x concentrated no standard addition; Hg with flameless AA, Se with diaminobenzidine |
| Biochemical Oxygen Demand | Measured |
| Coliform | Measured |
| Standard Plate Count | |
| Gasses | Varian No. 2720, silica gel and molecular sieve for $CO_2$, $N_2O_2$, $CH_4$ |
| Miscellaneous | Polarographic DO meter,settleable solids |

### State of New Jersey, Bureau of Solid Waste (1974)

| Parameter | Method |
|---|---|
| pH | Glass electrode column |
| Oxidation/Red. Poten. | N/A |
| Conductivity | N/A |
| Total Solids, Volatile | 105°C and 550°C |
| Suspended Solids, Volatile | N/A |
| Chemical Oxygen Demand | Dichromate reflux |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | |
| Chlorides | Argentometric |
| Sulfates | Turbidimetric or technicon |
| Phosphate | $SnCl_2$ or technicon autoanalyzer |
| Alkalinity | N/A |
| Nitrate | Phenol disulfonic acid or technicon autoanalyzer |
| Nitrite | N/A |
| Ammonia-N | Direct nesslerization |
| Na, K | |
| Ca, Mg | N/A |
| Hardness | EDTA |
| Heavy Metals | Hg flameless AA, As with Agdiethyl dithiocarbamate, Cd with dithizone Cr with diphenylcarbazide; Pb, Ni, Zn with AA, Cu with bathocuproine, Fe with tripyridine method, Mn with periodate, Se with diaminobenzidine |
| Biochemical Oxygen Demand | Seeded and azide modification |
| Coliform | Total fecal; also fecal streptococcus |
| Total Plate Count | N/A |
| Gasses | N/A |
| Miscellaneous | Color with chloroplatinate method ether solubles, chlorinated hydrocarbons, phenols, CN distillation and pyridine pyrazolore |

Department of Health, State of New York (1974)

| Parameter | Method |
|---|---|
| pH | Glass electrode, Beckman zeromatic |
| Oxidation/Red. Potent. | N/A |
| Conductivity | Beckman RC-16B2 |
| Total Solids, Volatile | N/A |
| Suspended Solids, Volatile | Glass fiber filter at 105° C, ignition at 550° C |
| Chemical Oxygen Demand | Simplified COD, colorimetric determination of excess dichromate |
| Total Organic Carbon | N/A |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | Kjeldahl digestion and titration |
| Chlorides | Thiocyanide method, Technicon Autoanalyzer |
| Sulfates | Methylthymol blue, Technicon Autoanalyzer |
| Phosphate | Persulfate digestion,ascorbic acid, Technicon Autoanalyzer |
| Alkalinity/Acidity | Titration to pH 4.5 |
| Nitrate | N/A |
| Nitrite | Sulfanilic Acid |
| Ammonia-N | Indophenol blue, Technicon Autoanalyzer |
| Na, K | AA, Varian Tectron |
| Ca, Mg | AA |
| Hardness | EDTA titration |
| Heavy Metals | AA; As with diethyldithiocarbamate |
| Biochemical Oxygen Demand | Seeded, yellow spring DO meter |
| Coliform | N/A |
| Standard Plate Count | N/A |
| Gasses | N/A |
| Miscellaneous | F with specific ion electrode |

### VTN Seattle (1974)

| Parameter | Method |
|---|---|
| pH | Combination glass electrode Sargent Expanded scale pH meter |
| Oxidation/Red. Poten. | N/A |
| Conductivity | N/A |
| Total Solids, Volatile | Dried at 103°C, 30 min at 600°C |
| Suspended Solids, Volatile | Glass fiber filter, Reef Angel in gooch crucibles, dried at 105° C |
| Chemical Oxygen Demand | Dichromate reflux |
| Total Organic Carbon | Beckman gas TOC analyzer |
| Volatile Acids | N/A |
| Tannins, Lignins | N/A |
| Organic-N | Distillation, digestion and nesslerization |
| Chlorides | Argentometric, changed to mercuric nitrate |
| Sulfates | Turbidimetric |
| Phosphate | $SnCl_2$ |
| Alkalinity | Titration to pH 4.5; titration to pH 8.3 |
| Nitrate | Modified Brucine (EPA) |
| Nitrite | N/A |
| Ammonia-N | Distillation and nesslerization with Bausch and Lomb Spec-20 |
| Na, K | Calculated from AA |
| Ca, Mg | AA Perkin Elmer 305 |
| Hardness | Calculated from AA |
| Heavy Metals | N/A |
| Biochemical Oxygen Demand | Azide modification |
| Coliform | MPN |
| Total Plate Count | Tryptone glucose agar |
| Gasses | |
| Miscellaneous | Color with spectrophotometer; UV absorption with Beckman DS-2A<br>$H_2S$ with methylene blue, LAS with methylene blue |

# SECTION 13

# APPENDIX B

Survey and discussion of physical, chemical, and biological methods used by various investigators.

Emcon Assoc. (1974) County of Sonoma (1973)

| Parameter | Method | Rational |
|---|---|---|
| pH | Beckman electromate w/NiCd cells<br>Combination electrode | pH meter used in lab and in field. Results are good |
| Oxidation/Reduction Pot. | N/A | |
| Conductivity | Beckman/Solo Bridge<br>RB3 - U104 | Good results but not easily used in field. Have recently purchased Myron |
| Total Solids, Volatile | Drying to constant weight at 105° C, 1 hr at 550° C | TDS (not volatile) drying done on water bath, then in oven over night. Cooled in desiccator |
| Suspended Solids, Volatile | Glass fiber filter, 1 hr at 105° C, 10 min at 600° C | |
| Chemical Oxygen Demand | 20 ml sample, 10 ml 0.25 N $K_2Cr_2O_7$<br>30 ml $H_2SO_4$ with $Ag_2SO_4$ | |
| Total Organic Carbon | N/A | |
| Volatile Acids | Column partition chromatographic method | Tests need care for good reproducibility. GC method is preferable. |
| Tannins, Lignins | N/A | |
| Organic-N | Kjeldahl, titration | Method is very good and reproducible; foaming is only routine problem. |
| Chlorides | Mercuric nitrate mixed indicator | |
| Sulfates | $BaSO_4$ precipitation method with ignition | Ignition method seems best as it reduced organic precipitation interference |
| Phosphates | Sulfuric/nitric acid dig.; vanadomolybd. phosphoric acid method; read on Beckman DB. | Acid digestion with vanadate erratic results. Now changing to ascorbate method as it is not as sensitive to pH changes |
| Alkalinity, Acidity | Titration to pH 4.2 | |
| Nitrates | Brucine read on Beckman DB | Aeration caused erratic results; also poor heat control. Method is good and gives reproducible curves. Leachate coloration requires sample blanks always be used. |
| Nitrite | N/A | |
| Ammonia-N | Kjeldahl titration | Method is very good and reproducible; foaming is only routine problem |
| Na, K | AAS No additions dilution & turned flame | All photometric methods here are AAS. |
| Ca | EDTA titration, interference for heavy metals reduced by NaCN buffer | Mg is AAS; Ca is by EDTA but will go to AAS soon. |
| Mg | AAS | |
| Hardness | Total EDTA | Total hardness is EDTA. CN does not reduce all problems |
| Heavy Metals | 5 ml 1:1 $HNO_3$ added to 1 ℓ sample; atomic absorption | |

Emcon Assoc. (1974) County of Sonoma (1973

| Parameter | Method | Rational |
|---|---|---|
| Biochemical Oxygen Demand | Seeding fresh sewage seed. | Samples must be highly diluted; some problems with toxicity in some leachates |
| Coliforms | Presumptive test with lactose broth confirmed test with boric acid lactate broth, multiple tube dilution | Coliform test done by a subcontracting lab. |
| Total Plate Count | N/A | |
| Gasses | Varian 90-P; TC:1'Silica gel at 80° followed by 20' Mixed Mol Sieve external for $CO_2$, $CH_4$, $N_2$, $H_2S$, $O_2$ | Columns must be activated for adequate separation. |

### Engineering-Science (1974)

| Parameter | Method | Rational |
|---|---|---|
| pH | Glass electrode | Universal practice |
| Oxidation-Reduction Pot. | Pt-Calomel electrode | Universal practice |
| Conductivity | Conductivity bridge | Universal practice |
| Total Solids, Volatile | Drying to constant weight | |
| Suspended Solids, Volatile | Glass fiber filters | G. F. paper easy to handle |
| Chemical Oxygen Demand | Dichromate reflux | Accurate and precise |
| Total Organic Carbon | N/A | |
| Volatile Acids | N/A | |
| Tannins, Lignins | N/A | |
| Organic-N | Kjeldahl, titration | Best method |
| Chlorides | Mercuric nitrate method | No need for new method |
| Sulfates | Gravimetric with ignition of residue | No need for new method |
| Phosphates | Vanadomolybdate phosphoric acid method | Best method |
| Alkalinity, Acidity | Potentiometric titration to pH 4.5<br>phenolphthalein titration | |
| Nitrates | Brucine | Data shows it as best method |
| Nitrites | Sulfanilic acid method | Only method |
| Ammonia-N | Kjeldahl, titration | Best method |
| Na, K | Flame photometer, Coleman 20 | Simple and accurate |
| Ca, Mg | Atomic Absorption (Flame, LaO added) | Best to date |
| Hardness | Hach | Simple and accurate |
| Heavy Metals | Graphite furnace, atomic absorption<br>Hg - Cold Vapor | Best to date |
| Biochemical Oxygen Demand | Five days BOD with multiple dilutions<br>Azide modification | DO meters less reliable |
| Coliforms | MPN test | Simple and accurate |
| Total Plate Count | Standard plate count | Simple and accurate |
| Gasses | Gas chromatography, silica gel - molecular sieve | Best accuracy |

Foree and Reid (1972) Foree and Cook (1972) Foree (1974)

| Parameter | Method | Rational |
|---|---|---|
| pH | Corning Model 10 pH meter; glass electrode | |
| Oxidation/Reduction Pot. | N/A | |
| Conductivity | Beckman cond. meter RC-16B82 | Any standard conductivity cell would be satisfactory |
| Total Solids, Volatile | N/A | |
| Suspended Solids, Volatile | Glass fiber filter, GC-Whatman; 10 min at 580° C | After filtration with Whatman GF/C glass fiber suspended solids after constant weight at 103-105° C volatile suspended solids by burning for 10 min at 580° C, this gives essentially the same result as burning for 15 min at 550° C |
| Chemical Oxygen Demand | | *Standard Methods* COD test is the best measure of organic strength of leachate. Results are very reproducible |
| Total Organic Carbon | Beckman TOC analyzer IR-315 acidified sample | |
| Volatile Acids | Column partition chromatographic method | Produces good results; gives only total volatile acids concentration |
| Tannins, Lignins | N/A | |
| Organic-N | Kjeldahl | Microkjeldahl digestion |
| Chlorides | N/A | |
| Sulfates | N/A | The $BaSO_4$ technique works quite well. Leachate color could possibly cause trouble if a spectrophotometer is used instead of a nephelometer or turbidimeter |
| Phosphates | Sample dried with magnesium chloride and heated for 10 min at 600° C followed by acid digestion, $SnCl_2$ method[1] | Used the indicated method for a number of years and found it to work well. Is preferred over some of the other acid digestion methods. However, the persulfate digestion method seems to be the most widely accepted method for wastewater analyses, and would probably be the method of choice for leachates. |
| Alkalinity | Titration to pH 8.3 and 4.3 | Titration to inflection point of titration curve is more correct. Titration to pH 8.3 and 4.3 gives essentially the same results in most cases. |
| Nitrates | Specific ion electrode | Chosen for its ease. It produces reasonably accurate results, chloride interference is significant in leachate but is easily removed by precipitation; the specific ion electrode method is a viable alternative to the Brucine method |
| Nitrite | N/A | |

| | | |
|---|---|---|
| Ammonia-N | Nessler method after steam distillation | Steam distillation followed by Nesslerization; there is no difference between micro and regular Kjeldahl; nesslerization method has worked quite well and is preferred over titration; direct nesslerization for ammonia-N determinations will not generally work very well because of excessive interferences. |
| Na, K | AAS | |
| Ca | AAS | Atomic absorption for calcium, magnesium |
| Mg | | |
| Hardness | N/A | |
| Heavy Metals | AAS; Fe with colorimetric method and AAS | Atomic absorption for all heavy metals; low sensitivity for iron with atomic absorption |
| Biochemical Oxygen Demand | SM; Azide modifications; DO meter | Seeding is definitely called for in the BOD test because leachates are normally anaerobic and have low pH when collected thus potentially a low population of viable aerobic organisms; Winkler technique more reliable than DO determinations |
| Coliforms | Membrane filter technique | Use membrane filter techniques for both fecal and total coliform tests. Only fecal coliform analysis recommended; do not include total coliform |
| Total Plate Count | N/A | |
| Gasses | Fisher Hamilton gas partitioner | It works very well. There are other more sophisticated chromatographs which can be used if available. |

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[1] Sawyer, C. N., and McCarty, P. L. "Chemistry for Sanitary Engineers," McGraw Hill, New York, p. 518 (1967).

State Water Resources Control Board California (1974)

| Parameter | Method | Rational |
|---|---|---|
| pH | Glass electrode | Electrometric pH is most sensitive method and works well with colored and turbid solutions. Experience very satisfactory |
| Oxidation-Reduction Pot. | Pt and Calomel electrode | Platinum is inert and calomel is a good reference electrode. Experience is satisfactory |
| Conductivity | Leeds & Northrup conductivity meter | Experience is satisfactory |
| Total Solids, Volatile | Drying to constant weight | Satisfactory |
| Suspended Solids, Volatile | Glass fiber filter | Satisfactory |
| Chemical Oxygen Demand | Use of mercuric sulfate to complex chloride ion | |
| Total Organic Carbon | Beckman 915/215A | Satisfactory with acidified sample |
| Volatile Acids | Column partition chromatography and titration | Satisfactory |
| Tannins, Lignins | Molybdophosphoric acid | Satisfactory |
| Organic-N | Kjeldahl, titration | Satisfactory; total N is sum of ammonia-, organic-. |
| Chlorides | Titration with $HgNO_3$ using diphenyl carbazone indicator | |
| Sulfates | $Ba_2SO4$ precipitation method | Gravimetric after acidification to eliminate carbonates; satisfactory |
| Phosphates | Phosphomolybdic acid. Digestion accomplished by pressure cooking in autoclave | Satisfactory for total phosphate |
| Alkalinity, Acidity | Titration to equivalence points 5.1; 4.8; 4.5 | |
| Nitrates | Brucine method | Sensitive method. Excludes nitrites when sulfamic acid is used. Experience: accuracy and precision not the best |
| Nitrites | Diazotization with sulfamilamide and coupling with alpha naphthylenediamine[1] | |
| Ammonia-N | EPA method; distilled from borate buffer at pH 9[2] | Minimizes hydrolysis of amino acids; satisfactory |
| Na, K | Flame photometer and atomic absorption | |
| Ca | Ca by precipitation as oxalate and titration with $KMNO_4$. Mg by versene titration of filtrate. Also AA using La | Satisfactory |
| Mg | Ca by precipitation as oxalate and titration with $KMNO_4$. Mg by versene titration of filtrate. Also AA using La | Satisfactory |
| Hardness | Calculated from Ca and Mg expressed as $CaCO_3$ | |
| Heavy Metals | AA using heated graphite atomizer and emission spectroscopy; AA method of choice | |
| Biochemical Oxygen Demand | Multiple dilution seeded with settled sewage | Experience very satisfactory with reference samples |

[1] Strickland, J. D. H., and Parsons, T. R. "A Practical Handbook of Seawater Analysis" Bulletin by Fisheries Research Board of Canada, Ottawa (1968) p. 77.

[2] Environmental Protection Agency "Methods for Chemical Analysis of Water and Wastes," EPA-National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio, Report 16020-07171 (1971).

State Water Resources Control Board California (1974)

| Parameter | Method | Rational |
|---|---|---|
| Coliforms | Multiple tube fermentation | Leachate precludes efficient use of membrane filter methods |
| Total Plate Count | Standard Plate Count | Satisfactory |
| Gasses | N/A | |

Griffin; Illinois State Geological Survey (1974)

| Parameter | Method | Rational |
|---|---|---|
| pH | Metrohm glass electrode | Gives less drift in leachate then either Corning or Beckman electrodes. Meter used is not important |
| Oxidation-Reduction Pot. | Pt and Calomel electrode | Combination Orion 96-78 largest Pt surface area available as a combustion electrode |
| Conductivity | Beckman cond. meter | Beckman 2 ml pipette cell is less subject to interference from the walls of the vessel and takes less samples than Yellow Springs |
| Total Solids, Volatile | Drying to constant weight | |
| Suspended Solids, Volatile | .45 μ millipore membrane | |
| Chemical Oxygen Demand | Dichromate reflux | Volumetric finish easy and reliable |
| Total Organic Carbon | | |
| Volatile Acids | Hydroxyl amine acidic ferric chloride colorimetric test[1] | Requires small volume of sample and simple equipment |
| Tannins, Lignins | N/A | |
| Organic-N | Kjeldahl, titration | |
| Chlorides | Mercuric nitrate titration - diphenylcarboxyl indicator | Faster then electrode titration |
| Sulfates | $BaSO_4$ precipitation method | |
| Phosphates | Ascorbic acid | Color development is not time sensitive and determination is more convenient than $SnCl_2$ method |
| Alkalinity, Acidity | N/A | |
| Nitrates | Brucine method | |
| Nitrites | N/A | |
| Ammonia-N | Kjeldahl, titration | |
| Na, K | Atomic absorption, Cs added | |
| Ca, Mg | Atomic absorption | La added; Sr seemed contaminated when we tried to use it because it is so much cheaper than La |

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[1] Montgomery, H. A. C. et al. "The rapid colorimetric determination of organic acids and their salts in sewage sludge liquor," Analyst 87, 949 (1962).

Griffin; Illinois State Geological Survey (1974)

| Parameter | Method | Rational |
|---|---|---|
| Hardness | | |
| Heavy Metals | Atomic adsorption; Ni, Cr, Pb, Cd, Zn, Cu, Ag, Fe, Mn, Si, Al, $N_2O$ flame, B with methylene blue method | Atomic Absorption with background correction for elements below 230 Hg by NNA. Questionable high results with B analysis, carmine method would give better results. |
| Biochemical Oxygen Demand | N/A | |
| Coliforms | N/A | |
| Total Plate Count | N/A | |
| Gasses | | |

Ott; Lowell Techn. Institute

| Parameter | Method | Rational |
|---|---|---|
| pH | Orion Model 701 digital pH meter | Unit was available |
| Oxidation-Reduction Pot. | N/A | |
| Conductivity | N/A | |
| Total Solids, Volatile | Drying to constant weight at 105° C, 1 hr at 550° C | |
| Suspended Solids, Volatile | N/A | |
| Chemical Oxygen Demand | Modification of standard dichromate method - uses 0.5 N $K_2Cr_2O_7$ and reflux for 20 min | Time reduction |
| Total Organic Carbon | N/A | |
| Volatile Acids | Titration from pH 4 to 7[1] | |
| Tannins, Lignins | N/A | |
| Organic-N | N/A | |
| Chlorides | N/A | |
| Sulfates | N/A | |
| Phosphates | N/A | |
| Alkalinity, Acidity | Titration to inflection point of titration curve | |
| Nitrates | N/A | |
| Nitrites | N/A | |
| Ammonia-N | N/A | |
| Na, K | N/A | |
| Ca, Mg | Atomic absorption (Perkin Elmer Model 107) | Unit was available |
| Hardness | N/A | |
| Heavy Metals | Atomic Absorption (Perkin Elmer Model 107) | Unit was available |
| Biochemical Oxygen Demand | Seeding/Winkler DO titration | |
| Coliforms | N/A | |
| Total Plate Count | N/A | |
| Gasses | N/A | |

[1] Dilallo, R., and Albertson, O. E. "Volatile Areas by Direct Titration," JWPCF 33, 356 (1961)

Pavoni and Tittlebaum (1974)

| Parameter | Method | Rational |
|---|---|---|
| pH | Glass electrode, Corning Digital III pH meter | |
| Oxidation-Reduction Pot. | | |
| Conductivity | Yellow Spring | |
| Total Solids, Volatile | Drying to constant weight at 105° C<br>1 hr at 550° C | Accepted method |
| Suspended Solids, Volatile | Glass fiber filter, constant weight at 105° C, 1 hr at 550° C | Accepted method |
| Chemical Oxygen Demand | Dichromate reflux method | Accepted method |
| Total Organic Carbon | Beckman 915 TOC analyzer | Available equipment |
| Volatile Acids | Column partition chromatographic method | Reliable results obtained |
| Tannins, Lignins | N/A | |
| Organic-N | Kjeldahl, titration | |
| Chlorides | Titration with electrode | |
| Sulfates | $BaSO_4$ precipitation method | Rapid and accurate at concentrations less than 10 mg/l |
| Phosphates | Persulfate digestion and $SnCl_2$ method | Ease of method with reliable results |
| Alkalinity, Acidity | Titration to inflection point | Greatest accuracy and no color interference |
| Nitrates | N/A | |
| Nitrites | N/A | |
| Ammonia-N | Kieldahl, titration | High nitrogen concentrations |
| Na, K | N/A | |
| Ca, Mg | Atomic absorption | Greatest accuracy |
| Hardness | Calculated from concentrations | Greatest accuracy |
| Heavy Metals | Atomic absorption | Greatest accuracy |
| Biochemical Oxygen Demand | Seeding/no seeding, iodometric-titration method | Confidence in reliability of method |
| Coliforms | N/A | |
| Total Plate Count | N/A | |
| Gasses | | |

Pohland (1974)

| Parameter | Method | Rational |
|---|---|---|
| pH | Leeds Northrop pH meter model #7411 & Fisher glass (flow-type) & calomel electrodes | Good speed; accurate to ± 0.1 pH unit |
| Oxidation-Reduction Pot. | L & N meter model #7411 & Fisher platinium & reference electrode | Stable; accurate m.v. readings |
| Conductivity | YSI conductivity meter model #31 | Speed; accurate to ± 1% |
| Total Solids, Volatile | Ceramic evaporating dishes | Standardized; established results |
| Suspended Solids, Volatile | Filtration w/Gellinan glass fiber filters | Standardized; established results |
| Chemical Oxygen Demand | Digestion & dichromate - FAS | Standardized; established results |
| Total Organic Carbon | Beckman M-915 Total Organic Carbon Analyzer | Accurate IR readings ± 1%; limited by operator's injection technique |
| Volatile Acids | Hewlett-Packard Model 700-G.C. (w/ Carbowax 4000 60/80 mesh CW Acid washed-DMCS column) | Accuracy to 0.5%; trouble free if tests are performed routinely |
| Tannins, Lignins | N/A | |
| Organic-N | Technicon Autoanalyzer; continuous Auto digestor & Berthelot colorimetric reaction | Great speed for large number of samples; ± 1% accuracy for samples in 0-100 mg/l nitrogen range |
| Chlorides | Technicon Autoanalyzer; mercuric thiocyanite colorimetric reaction | Great speed for large number of samples; ± 0.5% accuracy for samples in 0.20 mg/l Cl range |
| Sulfates | Atomic Absorption Spectrophotometer (Perkin Elmer Model 303). | Excellent speed; accuracy to ± 0.05% |
| Phosphates | Technicon Autoanalyzer; molybdate-ANSA colorimetric reaction | Great speed for large number of samples; + 0.5% accuracy for samples in the 1-50 mg/l. |
| Alkalinity, Acidity | Titration curve w/L & N pH meter glass-reference electrodes & indicators | Accuracy to ± 2 mg/l as CaCO$_3$ |
| Nitrates | Technicon Autoanalyzer; sulfanilamide-hydrazine colorimetric reaction | Great speed for large number of samples; ± 0.5% accuracy in 0-1 mg/l NO$_3^-$ range |
| Nitrites | Technicon Autoanalyzer; sulfanilimide hydrazine colorimetric reaction | Great speed for large number of samples; ± 0.5% accuracy in 0-1 mg/l NO$_2^-$ range |
| Ammonia-N | Technicon Autoanalyzer; berthelot colorimetric reaction | Great speed for large number of samples; ± 1% accuracy for samples in 0-100 mg/l nitrogen range |
| Na, K | Atomic Absorption Spectrophotometer (Perkin-Elmer Model 303) | Excellent speed; accuracy to ± 0.05% |
| Ca | Atomic Absorption Spectrophotometer (Perkin-Elmer Model 303) | Excellent speed; accuracy to ± 0.05% |
| Mg | Atomic Absorption Spectrophotometer (Perkin-Elmer Model 303) | Excellent speed; accuracy to + 0.05% |
| Hardness | Chelation; titration w/EDTA | Accuracy to ± 2 mg/l |
| Heavy Metals | Atomic Absorption; Spectrophotometer (Perkin-Elmer Model 303) | Excellent speed; accuracy to ± 0.05% |
| Biochemical Oxygen Demand | 5-day seeding & Azide modification of iodometric DO | Standardized; established results/ eliminates N$_2$ species interference |
| Coliforms | N/A | |
| Total Plate Count | N/A | |
| Gasses | Fisher Gas Partitioner | Fast, versatile, good separation; accurate to ± 0.5% |

Ralph Stone (1974)

| Parameter | Method | Rational |
|---|---|---|
| pH | Analytical measurements pH meter | Instrument with limited capabilities, obtaining a newer Beckman |
| Oxidation-Reduction Pot. | N/A | |
| Conductivity | N/A | |
| Total Solids, Volatile | Drying to constant weight at 105° C, 1 hr at 550° C | |
| Suspended Solids, Volatile | Glass fiber filter, GFC Whatman, constant weight at 105° C, 1 hr at 550° C | |
| Chemical Oxygen Demand | Dichromate reflux | |
| Total Organic Carbon | N/A | |
| Volatile Acids | Column Partition chromatography | Messy, but results have been satisfactory |
| Tannins, Lignins | N/A | |
| Organic-N | Kjeldahl, titration | |
| Chlorides | Mercuric nitrate titration | |
| Sulfates | $BaSO_4$ precipitation | Hach turbidimeter |
| Phosphates | Persulfate digestion and $SnCl_2$ method | |
| Alkalinity, Acidity | Titration to methyl orange | |
| Nitrates | Brucine method | |
| Nitrites | N/A | |
| Ammonia-N | Kjeldahl, titration | |
| Na, K | N/A | |
| Ca | Either EDTA titration or atomic absorption, La added | |
| Mg | Either EDTA titration or atomic absorption, La added | |
| Hardness | EDTA titration | |
| Heavy Metals | Atomic absorption | |
| Biochemical Oxygen Demand | Hach manometric BOD apparatus | Not as accurate as the standard method. Results have generally been satisfactory. |
| Coliforms | MPN multiple tube fermentation | Either 5 or 3 tubes, depending on the number of samples. Dehydrated media used |
| Total Plate Count | N/A | |
| Gasses | $CO_2$, $CH_4$, $O_2$, $N_2$. Varian A90-P3 GC with Poropak Q and molecular sieve columns, filament detector | |